

NERL/ERD Publications

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Jan 1, 2001 - Dec 31, 2001

Presented Published

ABSTRACT/ORAL

Loux, N.T. The role of aqueous thin film evaporative cooling on rates of elemental mercury air-water exchange under temperature disequilibrium conditions. Presented at: Georgia Water Resources Conference, Athens, GA, March 26-27, 2001.

3/26/2001

Contact: Nicholas T. Loux

Abstract: The technical community has only recently addressed the role of atmospheric temperature variations on rates of air-water vapor phase toxicant exchange. The technical literature has documented that: 1) day time rates of elemental mercury vapor phase air-water exchange can exceed nighttime rates by a factor of 2 to 3, 2) diurnal air-water exchange rates for PCBs (a conservative tracer for dynamic environmental elemental mercury) can exceed nocturnal rates by 44%, and 3) atmospheric vapor phase organic compound and elemental mercury concentrations can be correlated with atmospheric temperatures. Loux (2000) developed a model for quantifying elemental mercury air-water exchange rates under variable atmospheric temperature conditions. Utilizing the two layer thin film exchange paradigm, the model is designed to estimate exchange rates under quiescent, low wind speed conditions. An assumption in this effort was that the temperature of the thin aqueous film dominating mercury vapor air-water exchange equals the atmospheric temperature. While this assumption is plausible under conditions of very low wind speeds and/or near 100% relative humidity, what effect would evaporative cooling have on the aqueous phase mass transport coefficient? Specifically, will evaporative cooling have a significant effect on rates of elemental mercury air-water exchange? This and other issues will be addressed.

Loux, N.T., and Washington, J.W. Errors in applying low ion-strength activity coefficient algorithms to higher ionic-strength aquatic media. Presented at: American Society for Testing and Materials 11th Symposium on Environmental Toxicology and Risk Assessment, Phoenix, AZ, April 2-4, 2001.

4/2/2001

Contact: Nicholas T. Loux

Abstract: The toxicological and regulatory communities are currently exploring the use of free-ion-activity- models as a means of reducing uncertainties in current methods for assessing metals bioavailability from contaminated aquatic media. While most practitioners would support the desirability of this objective, several technical questions remain to be addressed in achieving this goal. Mathematical algorithms relating dissolved salt concentrations to ionic activity coefficients range from the purely theoretical Debye-Huckel Limiting Law (suitable to ionic salt concentrations less than 0.001 molar) to semiempirical "robust" relationships (the Davies and Extended Debye-Huckel expressions; rated up to an ionic strength of 0.5 molar) to the Pitzer relationships (applicable at ionic strengths up to supersaturated salt solutions). Given that environmental aquatic systems may possess dissolved salt concentrations ranging from less than 0.01 molar (freshwater systems) to greater than 0.7 molar (marine systems), and that Pitzer relationships are not available for most trace ionic toxicants, the need for robust high ionic strength activity coefficient algorithms for trace toxicants is obvious. This work will provide a quantitative estimate of the errors associated with applying the Davies and Extended Debye-Huckel activity coefficient algorithms (both independently and in conjunction with the geochemical speciation model MINTQA2) to aqueous solutions at ionic strengths below and above 0.5 molar/molal. A quantitative assessment of the errors will be made and the prognosis for developing interim improvements will be discussed.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Loux, N.T. The effect of salinity on rates of elemental mercury air/water exchange. Presented at: International Workshop on Trends and Effects of Heavy Metals in the Arctic, McLean, VA, June 18-22, 2001.

6/18/2001

Contact: Nicholas T. Loux

Abstract: The U.S. EPA laboratory in Athens, Georgia is pursuing the goal of developing a model for describing toxicant vapor phase air/water exchange under all relevant environmental conditions. To date, the two-layer exchange model (suitable for low wind speed conditions) has been modified to account for the effects of environmental temperature disequilibrium conditions and evaporative cooling on rates of elemental mercury air/water exchange (Loux, 2000; Loux, 2001a; Loux, 2001b). One (of many) issue(s) remaining to be addressed in this effort includes the effect of salinity on elemental mercury air/water exchange rates. Elemental mercury exists as an uncharged dissolved gas when present in aqueous solution. As such, it is reasonable to expect the aqueous solubility of mercury to be sensitive to the same salting out phenomena observed with other neutral dissolved gaseous species. A traditional approach for quantifying the effect of salinity on solubility is the Setchenov relationship; a Setchenov relationship for elemental mercury was derived from data published in the peer-reviewed technical literature and its significance to air/water exchange rates in a previously simulated system was assessed to be less significant than: 1) diel variations in water column Hg concentrations, 2) diel variations in air/water temperature disequilibrium conditions, and 3) the effects of evaporative cooling on air/water exchange rates.

Baca, R.M. The influence of ecological and anthropogenic factors on patterns in the fish communities of the Albemarle-Pamlico Basin. Presented at: American Fisheries Society Annual Meeting, Phoenix, AZ, August 19-23, 2001.

8/19/2001

Contact: Robert M. Baca

Abstract: Data on fish abundance from the EPA, USGS, and states of North Carolina and Virginia were analyzed for patterns in the fish communities of the Albemarle-Pamlico Basin. The basin covers 72,500 square kilometers and five ecoregions in Virginia and North Carolina, including the watersheds of the Chowan, Roanoke, Tar-Pamlico, and Neuse Rivers. Cluster analysis separated fish communities into groups by combinations of river basin and ecoregion. Distinct groups were detected for the Middle Atlantic Coastal Plain independent of river basin, the Tar-Pamlico/Neuse Piedmont and Middle Atlantic Coastal Plain, the Chowan/Roanoke Piedmont, and the Chowan Southeastern Plains. Correspondence analysis was used to find patterns between human land-use and fish community structure within these groups. Data from the Multi-Resolution Land Characteristics project was used to describe the impact of humans around fish sample sites. In most cases, the first canonical variate further separated the fish communities along a gradient of low to high human impact, such as from forested/wetland areas to residential/industrial areas. This research is part of a larger initiative at EPA modeling how fish in the basin may respond to changes in land-use patterns by humans over a 50 year period.

Bird, S.L., Exum, L.R., Alberty, S.W., and Perkins, C. Estimating impervious cover from regionally available data. Presented at: US Environmental Protection Agency Regional Vulnerability Assessment Workshop, Research Triangle Park, NC, October 29-30, 2001.

10/29/2001

Contact: Sandra L. Bird

Abstract: The objective of this study is to compare and evaluate the reliability of different approaches for estimating impervious cover including three empirical formulations for estimating impervious cover from population density data, estimation from categorized land cover data, and to explore the value of basing estimation techniques on a combination of data sources.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Rashleigh, B. Effects of habitat degradation on biological endpoints in the South Fork Broad river basin, Georgia. Presented at: Georgia Water Resources Conference, Athens, GA, March 26-27, 2001.

3/26/2001

Contact: Brenda Rashleigh

Abstract: Many of the streams of the lower Piedmont ecoregion in Georgia have been negatively impacted to some degree by habitat degradation due primarily to sedimentation. The South Fork of the Broad River watershed has been designated as sediment impacted under Section 303(d) of the Clean Water Act. A comprehensive field monitoring program has been established for the South Fork watershed including the development of relationships of sedimentation and biotic endpoints. Biotic endpoints are recognized as an important indicators of this degradation. In this assessment constrained ordination is used to examine the relation of fish and benthic macroinvertebrate sample data to selected habitat measures taken at 13 sites in and adjacent to the South Fork Broad river basin. Habitat degradation is reflected in benthic macroinvertebrate communities as a decrease in the Clingers/Burrowers ratio, as well as an increase in the abundance of Ephemeroptera and Odonata. Habitat degradation is reflected in fish communities as a increase in sunfish and a shift in the composition of minnow species. Both fish and benthic macroinvertebrates appear to be influenced primarily by natural gradients, and secondarily by habitat quality. A better understanding of the role of sedimentation and habitat in structuring communities improves our ability to use these communities as measurement endpoints in watershed assessment.

Burke, Jr., R.A. Use of GC-MS/combustion/IRMS to identify and determine the stable carbon isotopic ratio of individual lipids. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Roger A. Burke

Abstract: A system that couples a gas chromatograph (GC) via a split to a quadrapole mass spectrometer (MS) and, through a combustion interface, to an isotope ratio mass spectrometer (IRMS) allows the simultaneous detection of electron impact mass spectra and stable carbon isotope ratio analysis of individual compounds separated on a single capillary column. The split is designed so that about 80% of the flow is diverted to the combustion/IRMS with the remainder going to the MS. This split ratio is generally adequate for compound identification and allows useful accuracy and precision of stable carbon isotopic analysis (0.5 to 2 parts per thousand). This system has been successfully used for about five years to analyze various mixtures of lipids. These lipid mixtures have included alkanes and polyaromatic hydrocarbons (PAH) resulting from the combustion of biomass materials, and the methyl esters of fatty acids derived from soil and sediment microorganisms.

Rashleigh, B., and Johnston, J.M. Simulation coastal plain stream fish community response to nonpoint source pollution using linked hydrologic-ecological models. Presented at: Ecological Society of America Meeting, Madison, WI, August 5-10, 2001.

8/5/2001

Contact: Brenda Rashleigh

Abstract: Nonpoint source pollution is the primary stress in many streams. Characteristic declines in stream fish communities are recognized in streams influenced by nonpoint source pollution, but the processes by which these declines occur are not well understood. Here, predicted time series of flow, sediment, nutrients, and temperature from the HSPF watershed model were used as input to the Aquatox ecological model to simulate effects of nonpoint source stressors on fish assemblages. The models were calibrated to Contentnea Creek in the coastal plain of North Carolina. Stream fish assemblages were most sensitive to changes in flow and temperature, and less sensitive to changes in sediment and nutrient loading. Increased flow lead to increased population sizes for algae and insects but decreased settling of detritus, which reduced food available to omnivores. Increased temperature altered seasonal abundance patterns of all taxa. Linked hydrologic-ecological models are useful for integrating multiple stresses with ecological interactions, assessing the response of stream fish communities, and projecting the outcomes of future landuse scenarios.

Jan 1, 2001 - Dec 31, 2001

Presented Published

8/5/2001

Wright, C.J., and Alberty, S.W. Characterization of land use in riparian areas within the Contentnea watershed of North Carolina. Presented at: Ecological Society of America Meeting, Madison, WI, August 5-10, 2001.

Contact: Christina J. Wright

Abstract: Characterization of land use in riparian areas within the Contentnea watershed of North Carolina. Wright, C.J., 1 and S.W. Alberty. 2 1 U.S. Environmental Protection Agency, Athens, GA 30605 USA; 2 OAO Corporation, Athens, GA 30605 USA. Legislation mandating riparian buffers for the improvement of surface water quality has become widespread throughout the United States. However, availability of data describing the current condition of riparian areas, particularly at a regional scale, is minimal. In response to this lack of data, many studies of riparian buffer systems rely upon regional databases to determine land use within legislated distances from local stream channels, with variable degrees of accuracy. To assess the accuracy of using regional databases for relatively small land areas, land use in riparian areas was characterized from the Multi Resolution Land Characterization (MRLC) database and from digital orthophotographs within a geographic information systems (GIS) framework. The stream network within the Contentnea watershed was taken from US-EPA Reach File 3 database. Analysis of land use/land cover within a standardized 30 meter riparian buffer and the MRLC database indicates the following land use categories: water (2.30%), commercial/residential (1.17%), bare ground (0.14%), forested/forested wetland (84.43%), and agricultural (11.96%). A riparian cover analysis tool was developed for digital orthophotograph analysis. Transects were established perpendicular to the Reach File 3 stream network at intervals of 200 m. Land use was recorded at points located 15 and 30 meters distant from the stream. Preliminary analyses of digital orthophotographs indicate the following land use categories: water (0.30%), commercial/residential (2.20%), bare ground (2.30%), forest/forested wetland (91.5%), and agricultural (3.70%).

Molina, M. Microbial diversity in surface sediments: a comparison of two estuarine continuums. Presented at: American Society of Limnology and Oceanography Aquatic Sciences Meeting, Albuquerque, NM, February 12-16, 2001.

2/14/2001

Contact: Marirosa Molina

Abstract: The microbial diversity in estuarine sediments of the Altamaha and Savannah Rivers in Georgia were compared temporally and spatially using phospholipid fatty acid (PLFA) analysis. Surface sediment samples collected along a salinity gradient were also analyzed for ATP, TOC, and C stable isotopes of sediments and individual PLFAs. Both the Savannah and Altamaha contained similar concentrations of total PLFAs and ATP. However, the Savannah contained higher concentrations of phototrophic indicators (16:1w3 and 20:5w3) and lower concentrations of i15:0, i16:0 and 10Me16:0 (Gram + bacteria). The Shannon Diversity Index indicated significant within river differences due to season, but no difference between rivers. During March and October 1997 (lowest diversity in both rivers) the sediment del 13C indicated areas of C3 deposition at the mouth (-27.6 per mil). The signal was more enriched in 13C (-16.8 to -21.5 per mil) at the mesohaline area, indicating higher inputs from marine and C4 sources. 13C-PLFAs indicated selective C utilization by specific groups of the microbial community. The data suggest that in these rivers, the quality of the natural fluctuation of organic C may be more important than anthropogenic influences in determining the diversity and structure of microbial communities in surface sediments.

Burke, Jr., R.A. Use of GC-MS/combustion/IRMS to identify and determine the stable carbon isotopic ratio of individual lipids. Presented at: Universidad Autonoma de Baja California, Ensenada, Mexico, October 9-13, 2001.

10/9/2001

Contact: Roger A. Burke

Abstract: Compound specific isotope analysis (CSIA) has been increasingly used in recent years to elucidate biogeochemical and environmental processes responsible for the composition and concentration of lipids in soil and sedimentary environments. To perform CSIA an isotope ratio mass spectrometer (IRMS) is typically interfaced to a gas chromatograph (GC) via a combustion interface (C). Systems with a second mass spectrometer for compound structural identification interfaced to the GC have been recently described [Meir-Augenstein et al., 1994; O'Malley et al., 1997; Hall et al., 1999] and will probably become more common in the future with improvements in hardware and software.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Johnston, J.M., and Crossley, Jr., D.A. Neglected components of biodiversity: soil oribatid mites, community structure and soil recovery. Presented at: Soil Ecology Society Conference, Pine Mountain, GA, May 20-23, 2001.

5/20/2001

Contact: John M. Johnston

Abstract: Oribatid mites are an abundant and diverse component of soils in regional pine forests, and are valuable in characterizing the biodiversity of these forested lands. We sampled oribatid mites using soil cores and leaf litterbags, in young aggrading forest stands. Comparing these two techniques showed that litterbags provided an adequate measure of community diversity. Recovery of biodiversity was evident even in heavily managed stands. The best predictor of oribatid species diversity was stand age; it was more important than soil type or moisture

Bird, S.L. Alternative futures of urbanization: a research demonstration across the Mid-Atlantic region. Presented at: International Association for Landscape Ecology Meeting, Tempe, AZ, April 27, 2001.

4/27/2001

Contact: Sandra L. Bird

Abstract:

Loux, N.T. Effective acidity constant behavior near zero charge conditions. Presented at: 222nd American Chemical Society National Meeting, Chicago, IL, August 26-30, 2001.

8/26/2001

Contact: Nicholas T. Loux

Abstract: Surface site (>SOH group) acidity reactions require expressions of the form: $K_a = [\text{>SOHn-1(z-1)}]aH + \text{EXP}(-DG/RT)/[\text{>SOHnz}]$ (where all variables have their usual meaning). One can rearrange this expression to generate an $A_{\text{effective}}$ acidity constant historically defined as: $Q_a = K_a \text{EXP}(DG/RT) = [\text{>SOHn-1(z-1)}]aH/[\text{>SOHnz}]$; effective acidity constant behavior can be used to probe interfacial energetics. Although deriving estimates of Q_a for monoprotic systems is straightforward, deriving estimates of Q_{a1} and Q_{a2} from biprotic systems is much more ambiguous. Two alternatives to the traditional pH_{zpc} extrapolation procedure will be introduced and tested with computer generated data of known accuracy. All three methods will be applied to experimental data published in the technical literature for the purpose of possibly explaining anomalous DG behavior in the pH_{zpc} region within the context of charging energies (Loux, 2000) and aggregation-derived experimental artifact.

Russo, R.C. Development of marine water quality criteria. Presented at: Third International Conference on Marine Pollution and Ecotoxicology, Kowloon, Hong Kong, June 10-16, 2001.

6/10/2001

Contact: Rosemarie C. Russo

Abstract: The U.S. Environmental Protectional Agency has developed guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. These guidelines provide the method for deriving water quality criteria, including minimum data base requirements, data evaluation procedures, and calculations. The guidelines have been in place for a long time, and states have used them to derive water quality standards for their waterbodies. More recent efforts have been directed towards the development of technical guidance based on the concept that bioassessment and biocriteria programs for estuaries and near coastal waters are interrelated and are critical components of comprehensive water resource protection and management. This is a holistic approach to protection and management, integrating biological assessments into traditional chemical and physical evaluations and augmenting the established water quality criteria. The method for deriving water quality criteria and the approach for biocriteria development for marine systems are described.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Russo, R.C., and Carousel, R.F. Eutrophication modeling capabilities for water quality and integration towards ecological endpoints. Presented at: Sixth International Symposium on Fish Physiology, Toxicology, and Water Quality, La Paz, B.C.S., Mexico, January 22-26, 2001.

1/22/2001

Contact: Rosemarie C. Russo

Abstract: A primary environmental focus for the use of mathematical models is for characterization of sources of nutrients and sediments and their relative loadings from large river basins, and the impact of land uses from smaller sub-basins on water quality in rivers, lakes, and estuaries for excessive algal blooms, low dissolved oxygen (hypoxia), and related fish kills. For such a comprehensive evaluation a linked modeling system is required consisting of models that will simulate constituents and processes necessary to evaluate nutrient budgets and cycles on land and in the aquatic environment. Modeled processes include hydrodynamics, sediment erosion and transport, water temperature, oxygen and BOD dynamics, inorganic and organic nutrients, growth/respiration of algae, specified species within each trophic level, and toxicity of pollutants to modeled organisms, indirect effects produced by changes in grazing and predation pressures, changes in decay rates and detritus and nutrient cycling, and dissolved oxygen. A pilot study conducted in the Tensas watershed, located in the northeast corner of the State of Louisiana, will be described. Water quality models were evaluated that provide full capabilities for simulating eutrophication, can be linked to watershed loading models for nutrients, and provide output that can be used to determine indications of ecological impairment with fish-health as an endpoint. A total of 80 water quality models were evaluated from which seven water quality models were identified as candidates for use in linking to watershed loading models for evaluating the impact of nutrients and sediment on water quality. An overview of the necessary processes for moving towards an ecological endpoint will be presented.

Opsahl, S.P., and Zepp, R.G. Photochemically-induced transformations of dissolved organic matter in riverine waters. Presented at: American Society of Limnology and Oceanography Aquatic Sciences Meeting, Albuquerque, NM, February 12-16, 2001.

2/14/2001

Contact: Richard G. Zepp

Abstract: We demonstrated that exposure of riverine water to natural sunlight initiated degradation and corresponding alteration to the stable carbon isotope ratio and biochemical composition of the associated dissolved organic carbon (DOC). Water samples were collected from two distinct river systems-the Satilla River which has high DOC concentrations, and the Altamaha River which has relatively low DOC concentrations. Approximately 21-29% of the DOC was remineralized to DIC during the incubations. The stable carbon isotope ratio of DIC that was produced was isotopically "light" relative to the initial DOC, leaving a residual fraction of DOC that was isotopically "heavy". Fractionation of carbon during photochemically-induced degradation of terrigenous DOC was selective for certain biochemical constituents. These results are consistent with shifts in the isotopic signature of DOC that are observed during the mixing of fresh-and marine waters, and we propose that photochemically-induced alterations are a significant factor in determining these changes.

Anderson, S.L., Zepp, R.G., Machula, J., Hansen, L.J., Cherr, G., and Mueller, E. Assessing UV irradiance in Caribbean reef coral and DNA damage in their coral and zooxanthellae. Presented at: American Society of Limnology and Oceanography Aquatic Sciences Meeting, Albuquerque, NM, February 12-16, 2001.

2/12/2001

Contact: Richard G. Zepp

Abstract: UV penetration into the water near coral reefs may be increasing as a consequence of global climate change. Calm waters associated with ENSO conditions can enhance stratification that increases the amount of photobleaching of chromophoric dissolved organic matter (CDOM) in surface waters, causing increased UV penetration. We are examining CDOM spectral and photochemical properties and UV penetration at Florida Keys reef sites and in the adjacent Hawk Channel. Initial characterization of CDOM sources and biological, chemical and physical processes affecting its distribution are underway. We have shown that CDOM at the reefs photobleaches, and that UV penetration above the thermocline is greater than below. Sources of CDOM may include seagrass beds and mangroves. Immunoblotting and immunolocalization procedures have been developed to evaluate UV-specific DNA damages (thymine dimers) in coral and zooxanthellae of *Porites porites*. Laboratory studies indicated a proportional response to increases in UV radiation. Diurnal variation in thymine dimers in coral collected from reef sites indicates that cycles of damage and repair vary among colonies. Damage to DNA is localized in both coral and zooxanthellae. These findings may help to determine whether UV irradiance plays a significant role in coral bleaching.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Pinto, A., Bustamante, M., Viana, L., Zepp, R.G., Burke, Jr., R.A., Molina, M., and Kisselle, K. Soil emissions of CO₂ and CO in tropical savannas of Central Brazil under different fire regimes. Presented at: Large Scale Biosphere-Atmosphere Experiment in Amazonia Open Meeting, Atlanta, GA, February 12-14, 2001.

2/12/2001

Contact: Richard G. Zepp

Abstract: The Cerrado is a tropical savanna in which herbaceous vegetation (mainly C₄ grasses) coexists with trees and shrubs. It covers more than two million square kilometers and accounts for 22% of the total area of Brazil. In general, cerrado soils are old, deep, well drained, well structured, acidic, have low fertility, and high iron and aluminum contents. Mean rainfall is 1500 mm per year with well-defined wet and dry seasons. The term Cerrado represents three general physiognomic types of vegetation reflecting variation in degree of tree cover: campo sujo (open, grass-dominated), cerrado stricto sensu (ss) and cerrado (closed forest). In campo sujo <10% of the soil surface is shaded, whereas in the closed forest >90% of the soil surface is shaded. The degree of soil shading in cerrado ss ecosystems is intermediate between that of campo sujo and cerrado. Extensive areas of Cerrado have been converted to pastures and grasslands by frequent burning or clearing. Our objective was to assess the soil fluxes of CO₂ and CO in Cerrado areas subjected to prescribed fires. Biological production of CO₂ in soils is derived from the decomposition of soil organic matter and from root respiration. CO is produced by photodegradation of litter and it can be consumed by microbial activity. The studies are focusing on two classes of Cerrado, campo sujo and cerrado ss, located at the research and ecological reserve operated by IGBE, 35 km south of Brasilia (15°56'S, 47°53'W). The burned areas have been subjected to prescribed fires every two years since 1992 at the end of the dry season (late September). The unburned areas have been protected from fire for the last 26 years. A water addition experiment at unburned campo sujo was carried out in August 2000 (middle of dry season). The soil of the campo sujo areas is classified as Latossolo Vermelho-Amarelo (red-yellow Latosols, Brazilian Soil Classification) while Latossolo Vermelho-escuro (dark-red Latosols) are found in the cerrado ss. The measurements have been carried out since September 1999. The input of organic matter, microbial activity and soil moisture were pointed out as important variables affecting the soil respiration in Cerrado soils. The highest flux was found during the wet season (5.57 mol CO₂ cm⁻² s⁻¹) and the lowest during the dry season (1.62 mol CO₂ cm⁻² s⁻¹). On campo sujo plots, burned area showed high soil respiration on wet season (October 1999, April and September 2000) and on dry season there is no difference between burned and unburned areas. The grasses are more dominant in the burned area, and their roots could have an important contribution for soil respiration. The unburned cerrado showed higher soil respiration than burned cerrado and unburned campo sujo areas. The highest addition of organic matter on unburned cerrado could explain the higher soil respiration, and it contributes to higher activity of microorganisms. The addition of water during the dry season showed a stronger effect on soil respiration than the fire treatment. After 30 min of the water addition, the flux increased from 1.4 mol CO₂ cm⁻² s⁻¹ to 6.6 mol CO₂ cm⁻² s⁻¹, while no differences were observed before and after fire. The organic matter is also important for control of CO emissions. The unburned plots (high density of woody plants) showed the highest fluxes of CO. The main period of this production was on dry season, when the canopy was more open (higher UV incidence) and the amount of litter is high.

Zepp, R.G. Photoreactions in surface waters and their role in biogeochemical cycles. Presented at: American Society of Limnology and Oceanography Aquatic Sciences Meeting, Albuquerque, NM, February 12-16, 2001.

2/14/2001

Contact: Richard G. Zepp

Abstract: During the past decade significant interest has developed in the influence of photochemical reactions on biogeochemical cycles in surface waters of lakes and the sea. A major portion of recent research on these photoreactions has focused on the colored component of dissolved organic matter, referred to as CDOM. Photodegradation of CDOM contributes to loss of its UV and visible absorbance and fluorescence. Such "photobleaching", through interactions with climate-sensitive processes such as stratification, enhances the penetration of harmful UV-B radiation into surface waters and can influence the remote sensing of ocean color. In addition to these spectral effects, photoreactions of CDOM alter its biological availability and isotopic composition. Photochemical reactions in surface waters also enhance the cycling of metals such as iron, manganese, copper, and mercury, and result in the direct production of carbon dioxide, carbon monoxide, volatile hydrocarbons, nitrogen oxides, and sulfur-containing gases. This talk will use selected case studies to illustrate approaches that are being used to investigate these intriguing photoreactions in the laboratory and field.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Kisselle, K., Zepp, R.G., Burke, Jr., R.A., Pinto, A., and Bustamante, M. Photochemical effects on NO_x and CO emissions in a Brazilian savanna. Presented at: Ecological Society of America Meeting, Madison, WI, August 5-10, 2001.

8/5/2001

Contact: Richard G. Zepp

Abstract: Land clearing and burning in the tropics often results in increased solar irradiation of soil and surface organic matter. This increased light exposure may impact the emissions of nitrogen oxides (NO_x) and carbon monoxide (CO), trace gases that play an important role in tropospheric chemistry. Our objective in this study was to quantify the effect of light on these trace gas emissions at selected sites located in the Cerrado (savanna) in central Brazil. Two native vegetation types (cerrado sensu stricto and campo sujo) with or without recent burning, and a pasture site were studied. Gas measurements were made in the field using either clear, or covered (opaque), Pyrex chambers sealed on the soil surface. Laboratory studies of surface litter allowed gas emissions measurements while controlling the light wavelength and intensity and the temperature. Field NO_x flux measurements using clear chambers were higher than when using opaque chambers (approximately 4-7 times higher in burned sites; 2 times higher in the unburned native grassland and pasture). Immediately after burning, CO emissions from soils and charred surface organic matter increased in the cerrado, where 30 days after the fire, daytime CO emissions were over 10-fold higher than those from the unburned cerrado (812.8 x 10⁹ molecules cm⁻² s⁻¹ vs. 76.8 x 10⁹ molecules cm⁻² s⁻¹). The increase in CO production occurred both in light and dark chambers, suggesting that the fire created thermally-reactive precursors.

Bustamante, M., Pinto, A., Viana, L., Nardoto, G., Zepp, R.G., Burke, Jr., R.A., Molina, M., and Kisselle, K. Effects of prescribed fires on nitrogen fluxes in savanna formations of Central Brazil. Presented at: Large Scale Biosphere-Atmosphere Experiment in Amazonia Open Meeting, Atlanta, GA, February 12-14, 2001.

2/12/2001

Contact: Richard G. Zepp

Abstract: Savanna ecosystems are controlled by the interactions between water and nutrient availability. The savannas of Central Brazil (Cerrado) are the second most extensive plant formation in tropical South America with two million km² of area. The Cerrado landscape contains different combinations of diverse vegetation types: 1. cerrado?o ? medium to tall woodlands with closed or semi-closed canopies; 2. cerrado (restricted sense) ? savanna woodland of low trees or shrubs and 3. campo sujo ? open savanna with scattered trees or shrubs. Large transformations in the composition, structure and functioning of Cerrado ecosystems are expected to occur due to global climate and land-use changes. Extensive areas of Cerrado have been converted to pastures and grasslands by frequent burning or clearing. Our objective was to determine the effect of prescribed fires on the N-fluxes in campo sujo and cerrado (restricted sense) areas. The study has been carried out at the Ecological Reserve of the Instituto Brasileiro de Geografia e Estatística, 35 km south of Brasília (15° 56' S, 47° 51' W). The burned areas have been subjected to prescribed fires every two years since 1992 at the end of the dry season (late September). The unburned areas have been protected from fire for the last 26 years. The soil of the areas is classified as Oxisols. N mineralization rates were measured using in situ soil incubations (0-5 cm depth) in PVC cores. Soils were collected at the beginning of incubation period and one month later. Soil samples were collected for determination of pH (H₂O and KCl 1N) and water content. Soil microbial biomass was determined by the chloroform fumigation-incubation method. Fluxes of NO (dynamic chambers) and N₂O (static chambers) were measured at the four sites since September 1999. Four bases were sampled at each area. The soil water content was lower in the burned areas for both vegetation types. An increase of soil pH with the burning treatment was observed only for the cerrado area. The results suggested that the peak in microbial activity occurred with the first rain events, with an initial period of immobilization (increase of microbial biomass) followed by a period of mineralization. Nitrification rates were low for both vegetation types. In general, the N mineralization rates observed are similar to those determined for other seasonal ecosystems but lower than the rates found for tropical forests. Both treatments (burned and unburned) presented the same pattern for mineralization / immobilization but the burned areas presented lower availability of inorganic-N. There are no differences of NO fluxes between the plots, and the mean was 0.5 ng NO-N cm⁻²·h⁻¹ over dry season. Rain events promote pulses of NO emissions but this effect was short-lived. The fluxes of N₂O were very low in all plots. N₂O fluxes could not be detected in the unburned cerrado.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Zepp, R.G., White, E., and Vaughan, P.P. Influence of dissolved organic matter on agrochemical photoreactions in aquatic environments. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Richard G. Zepp

Abstract: Pioneering studies by Don Crosby and co-workers demonstrated that the sunlight-induced dissipation of agrochemicals in water often is strongly affected by natural constituents in the water such as nitrate and dissolved organic matter. In this presentation, the focus is on the role played by the colored component of dissolved organic matter, referred to as CDOM, in (a) controlling the availability of solar UV radiation in aquatic systems and (b) initiating indirect agrochemical photoreactions. CDOM, which is a mixture of lignocellulose-derived polyelectrolytes that are derived mainly from the decay of terrestrial vegetation, constitutes the majority of the organic carbon in most freshwater, estuarine and coastal environments. On irradiation, CDOM and its complexes with metals such as iron, produce excited state and reactive oxygen species that mediate indirect reactions. This talk will discuss recent approaches that are being used to study these intriguing photoreactions in the laboratory and field with particular emphasis on factors affecting the production of hydroxyl radicals.

Zepp, R.G. Interactions of solar ultraviolet radiation and dissolved organic matter in freshwater and marine environments. Presented at: Lehigh University - Invited Speaker, Bethlehem, PA, March 8, 2001.

3/8/2001

Contact: Richard G. Zepp

Abstract: Solar radiation provides the primary driving force for the biogeochemical cycles upon which life and climate depend. Recent studies have demonstrated that the absorption of solar radiation, especially in the ultraviolet spectral region, results in photochemical reactions that can have significant effects on the environmental cycling of carbon, oxygen, sulfur, and various trace metals in the environment. Other research has shown that photoreactions help cleanse the environment of the waste materials derived from human activities. In this presentation, selected current research results on the photochemical reactions in aquatic environments and on environmental surfaces are presented. First, photochemical reactions of organic matter and metal-organic complexes are considered. Then, rate equations and mechanisms for these photoreactions are described, including recent studies of the behavior of carbonyl excited states in aqueous media. Finally, modeling approaches are presented for the extrapolation of laboratory and field experiments to larger regional and global scales. The presentation is not intended to provide a comprehensive review of environmental photochemistry but rather to provide a taste of the exciting studies that are taking place in this area and the types of measurement approaches and concepts that are being applied. A significant portion of the photochemistry that occurs in aquatic environments is associated with the colored component of dissolved organic matter, referred to as CDOM. CDOM, which is a mixture of lignocellulose-derived polyelectrolytes that are derived mainly from the decay of terrestrial vegetation, constitutes the majority of the organic carbon in many lakes, rivers, and coastal waters. Photodegradation of CDOM results in loss of its UV and visible absorbance and fluorescence, a process referred to as "photobleaching," changes in the biological availability of its carbon- and nitrogen- containing constituents, and production of carbon dioxide, carbon monoxide, volatile hydrocarbons, and sulfur-containing gases (Figure 1). Photochemical production rates of dissolved inorganic carbon (DIC) from CDOM generally are at least an order of magnitude greater than those of other known photoproducts. However, a recent study has shown that the rates and quantum efficiencies for formation of biologically-labile photoproducts (compounds that are readily assimilated by bacteria) from CDOM are about the same as those observed for DIC photoproduction (Miller et al, personal communication). Organic complexes with metals (e.g. iron, copper, mercury) also are involved in environmental chemistry in aquatic environments, either via direct photoreactions of the complexes or reactions of the complexes with reactive oxygen species that are produced photochemically. Iron is involved in the photooxidation of CDOM in some freshwater ecosystems, such as the rivers that drain into the Atlantic Ocean and the Gulf of Mexico in the coastal U.S.A. The addition of strong $Fe(II)$ chelating ligands, such as fluoride, to such river waters can significantly reduce CDOM photodegradation rates, presumably by reducing concentrations of photoreactive Fe -CDOM complexes that participate in photoredox reactions or that catalyze free radical oxidation of the CDOM. Moreover, the environmental cycling of mercury is affected by photochemical reactions in the photic zone of aquatic

Jan 1, 2001 - Dec 31, 2001

Presented Published

Bailey, G.W. Hypoxia effect on the transformation, speciation, bioavailability and toxicity of chemical contaminants in the hypoxic zone. Presented at: Sixth International Symposium on Fish Physiology, Toxicology, and Water Quality, La Paz, B.C.S., Mexico, January 22-26, 2001.

1/22/2001

Contact: George W. Bailey

Abstract: This Symposium seeks to understand the direct effect of hypoxia on aquatic biota at the individual population, and the ecosystem levels. Another concern, however, is the indirect effect of varying oxygen levels on the thermodynamics and kinetics of biogeochemical processes and the effect of these changes on the transformations, speciation, bioavailability and toxicity of particulate-bound or dissolved forms of inorganic and organic contaminants as they pass through or reside in the hypoxia water column and in the underlying sediment. The basic tenets of redox chemistry are presented and reviewed. The redox potential (Eh) is used as a tool to assess the speciation of redox sensitive metals -- Cr, Fe, Mn, Cu, Ni, Zn, Cd, Pb, Hg -- and metalloids --As, S, and, Se-- and the transformation rates of organic C-, N-, P-, S-, constituents in both organic matter and in anthropogenic chemicals both in the hypoxic water column and the underlying sediment. Both literature findings and calculations from MINTEQA2, a geochemical equilibrium model, will be used to make the individual evaluations. Possible adverse effects of that redox-sensitive chemically active forms on aquatic biota present in the hypoxic zone will be presented.

Sawunyama, P., and Bailey, G.W. DFT study of the hydrolysis of some s-triazines. Presented at: 53rd Annual Meeting of the Southeastern Region of the American Chemical Society, Savannah, GA, September 23-26, 2001.

9/23/2001

Contact: George W. Bailey

Abstract: The acid-catalyzed hydrolysis of atrazine and related 2-chloro-s-triazines to the corresponding 2-hydroxy-s-triazines was investigated using the B3LYP hybrid density functional theory method. Gas-phase calculations were performed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G* level of theory. Gas-phase proton affinities, relative free energies of hydrolysis, enthalpies of hydrolysis, and activation energies were obtained. Proton affinities varied somewhat for different sites of protonation of atrazine (i.e., heterocyclic ring N1, N3, N5, and the side chain amine N atoms). N1 site exhibits the highest proton affinity (227.0 kcal mol⁻¹) whereas side chain amine N atoms show the least proton affinity (ca. 209.3 kcal mol⁻¹). The keto form of protonated hydroxyatrazine is 5.0 kcal mol⁻¹ more stable than the enol form. Aqueous solvation effects were examined using Self-Consistent Reaction Field methods (SCRF). Structures were optimized at the B3LYP/6-31G* level using the Onsager model and solvation energies were calculated at the B3LYP/6-311++G(d,p) level using the isodensity surface polarizable continuum model (IPCM). The extent of solvent stabilization was greater for ionic species than neutral species. Likewise, solvation reduced the hydrolysis barrier of atrazine by 8.6 kcal mol⁻¹.

McCutcheon, S.C. Chlorinated solvent plume control. Presented at: North Atlantic Treaty Organization Advanced Study Institute Innovative Approaches to the On-Site Assessment and Remediation of Contaminated Sites, Prague, Czech Republic, May 24 - June 2, 2001.

5/24/2001

Contact: Steven C. Mccutcheon

Abstract: This lecture will cover recent success in controlling and assessing the treatment of shallow ground water plumes of chlorinated solvents, other halogenated organic compounds, and methyl tert-butyl ether (MTBE).

Jan 1, 2001 - Dec 31, 2001

Presented Published

Ambrose, Jr., R.B., and Wool, T.A. Modeling mercury fate in seven Georgia watersheds. Presented at: Workshop on the fate, transport, and transformation of mercury in aquatic and terrestrial environments, West Palm Beach, FL, May 8-10, 2001.

5/8/2001

Contact: Robert B. Ambrose

Abstract: Field and modeling studies were conducted in support of total maximum daily loads (TMDLs) for mercury in six south Georgia rivers and the Savannah River. Mercury is introduced to these rivers primarily by atmospheric deposition, with minor point source loadings. To produce mercury TMDLs in these rivers, the GIS-based Watershed Characterization System (WCS) and a mercury delivery spreadsheet were developed and applied with the water pollutant fate model WASP5. Together, these models calculate mercury buildup in watershed soils, loading and delivery through the watershed tributary system, and mercury fate in the mainstem rivers. Site specific mercury data are required for model parameterization. These models were applied to the seven rivers and their watersheds, and checked against survey data gathered during very dry conditions in June and July, 2000. Despite environmental variability and scientific uncertainties, calculated mercury concentrations in soils, sediment, and water compared reasonably well with the observed data in most watersheds. The accuracy of these model predictions within and among these watersheds is described. Sensitivity analyses point to those processes and parameters controlling mercury fate in these river systems, including atmospheric deposition, impervious watershed area, soil reduction rate constant, tributary reduction rate constant, and tributary methylation status. Future development should focus on mercury transport and transformation reactions in the tributary systems.

Garrison, A.W., and Ellington, J.J. Analysis and fate of enantiomers of pesticides and other environmental pollutants. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Arthur W. Garrison

Abstract: Up to 25% of pesticides and other environmental pollutants are chiral and exist as sets of mirror image isomers, or enantiomers, that usually differ in their microbiological transformation rates and toxicities. To provide for more accurate risk assessment of these chiral pollutants it is, therefore, important to determine the relative biotransformation rates of their enantiomers so as to predict their persistence and occurrences in the environment and to estimate their relative toxicities. These studies require enantiomer separation techniques based on chiral chemistry. We have adapted and applied such separation techniques using high pressure liquid chromatography, gas chromatography and capillary electrophoresis. Examples will be shown of the separation of the enantiomers of organophosphorus, organochlorine, imidazolinone, phenoxyacid and other classes of pesticides, as well as of PCBs and other environmental pollutants. In addition, applications of these separation techniques to determine the environmental occurrences of enantiomers and the enantioselectivity of microbial transformation of chiral pollutants will be discussed.

Garrison, A.W. Separation of enantiomers of environmental pollutants. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Arthur W. Garrison

Abstract: Chiral environmental pollutants exist as sets of 2 (or more) enantiomers - mirror image isomers that are identical in all physical and chemical properties except when reacting with other chiral entities such as enzymes and other chiral molecules. This exception give rise to differences in microbiological transformation rates and toxicities of the enantiomers. It is, therefore, important to understand the relative biotransformation rates of enantiomers so as to predict their persistence and occurrences in the environment, and to study their relative toxicities. Coupling this persistence and toxicity data should allow more accurate risk assessment of pesticides and other pollutants. In order to study the occurrence, fate and toxicity of enantiomers, it is necessary to use separation techniques based on chiral chemistry. We have developed and adapted such techniques to high pressure liquid chromatography, gas chromatography and capillary electrophoresis instrumentation. Examples will be shown of the separation of the enantiomers of organophosphorus, organochlorine, imidazolinone, phenoxyacid and other classes of pesticides, as well as of PCBs and other environmental pollutants. In addition, applications of these separation techniques to determine the environmental occurrences of enantiomers and the enantioselectivity of microbial transformation of chiral pollutants will be illustrated.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Garrison, A.W. Capillary electrophoresis for enantiomer separation and measurement of enantioselectivity of chiral pollutants in the environment. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Arthur W. Garrison

Abstract: Chiral pollutants exist as 2 species, -- enantiomers - that have identical physical and chemical properties except when they interact with enzymes or other chiral molecules; then they usually react selectively. This enantioselectivity results in different rates of microbial transformation and differences in toxicity of the 2 enantiomers. To make more accurate risk assessments, it is necessary to understand the relative persistence and effects of the enantiomers; it follows that this understanding depends upon the ability to separate the enantiomers. Enantiomeric separation can be accomplished by the use of chiral columns in GC and BPLC, and by chiral selectors in capillary electrophoresis (CE). This presentation will describe techniques for enantiomer separation by CE, and show applications to environmental problems. For example, we have applied CE with cyclodextrin selectors to the enantiomeric analysis of hundreds of environmental samples spiked with an organophosphorus pesticide (crufomate) and a phenoxyacid herbicide (dichlorprop) to follow the enantioselective microbial transformation kinetics. We have also used CE to follow the enantioselective loss of bromochloroacetic acid spiked into several surface water samples. The advantages and disadvantages of CE for environmental analysis of chiral pollutants will be discussed.

Bailey, G.W., and Sawunyama, P. The integrated use of computational chemistry, scanning probe microscopy, and virtual reality to predict the chemical reactivity of environmental surfaces. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: George W. Bailey

Abstract: In the last decade three new techniques scanning probe microscopy (SPM), virtual reality (YR) and computational chemistry have emerged with the combined capability of a priori predicting the chemical reactivity of environmental surfaces. Computational chemistry provides the capability to study the chemical structure, dynamic behavior, and calculate the binding energies of environmental surfaces for chemical contaminants. SPM provides the capability at the atomic scale of resolution to investigate the structure and morphology of environmental surfaces and surface complexes. YR software and animated computer graphics enhance our capability to visualize and interpret 3-D structures and surfaces. We will present SPM images and YR graphics of muscovite, rutile, lignin, lignin-carbohydrate complexes, cyclodextrins, organo-mineral aggregates, and the outcome of molecular mechanical conformational calculations and molecular dynamics and ab initio simulations of these surfaces and of pesticide-organomineral aggregate interactions.

Collette, T.W., and Williams, T.L. Raman analysis of fertilizer and plant tissue extracts for perchlorate contamination. Presented at: Eastern Analytical Symposium, Atlantic City, NJ, October 1-4, 2001.

10/1/2001

Contact: Timothy W. Collette

Abstract: Recently, we and others found perchlorate at high levels (approximately 500 - 8000 mg/kg) in ~ 90% of 25+ fertilizer products (primarily lawn-and-garden type) with no known link to mined nitrate-bearing Chilean ore. This ore is used, albeit in small scale, in fertilizer production and is the only naturally-occurring material known to contain perchlorate as a trace component. Perchlorate contamination has emerged as an environmental concern since its discovery in some California water supplies in 1997 and because of its potential to affect the function of the thyroid gland. These fertilizer products were acquired over the period of November 1998 to January 1999 at 5 locations across the U.S. However, we have subsequently analyzed more than 20 similar products, which were acquired after May 1999. Some of these were the same products (although not the same lots) as those previously sampled. Most of these more-recent products do not contain detectable levels of perchlorate. Therefore, all of our results, and the results of others, suggest that the contamination of the earlier products was an episodic (if not singular) event. Nonetheless, there is an ongoing need for robust analytical methods for rapid and definitive analysis of perchlorate in complex matrices such as extracts of fertilizers and, also, plant materials, because some plants have been shown to take-up perchlorate when it is present in soil or irrigation water. We will describe the unique merits of analysis by Raman spectroscopy, without the need for prior chromatographic separation, to meet this need.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Ellington, J.J., and Evans, J.J. Method for the determination of perchlorate anion in plant and solid matrices by ion chromatography. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: James J. Ellington

Abstract: A standardized method for the analysis of perchlorate in plants was developed, based on dry weight, and applied to the analysis of plant organs, foodstuffs, and plant products. The procedure greatly reduced the ionic interferences in water extracts of plant materials. Ion chromatography (IC) on an AS16 anion exchange column was used for separation of perchlorate from the ionic matrix. The method will be described in detail including the difficulties encountered and overcome through the use of various sorbents and techniques. Plant materials studied included 12 fruits and vegetables, tobacco, and salt cedar. The method detection limit ranged from 0.16 ppm for cucumber to 1.10 ppm for sweet corn. In addition to food matrices samples of vegetation and soil from the Las Vegas wash, which has a historical record of contamination with perchlorate, were analyzed. The method, based on analysis by IC, will be compared to other methods of analysis based on mass spectrometry, capillary electrophoresis, and Raman spectroscopy.

Ambrose, Jr., R.B., and Wool, T.A. Modeling tools used for mercury TMDLs in Georgia rivers. Presented at: Georgia Water Resources Conference, Athens, GA, March 26-27, 2001.

3/26/2001

Contact: Robert B. Ambrose

Abstract: The Clean Water Act and associated regulations require each State to identify waters not meeting water quality standards applicable to their designated uses. Total maximum daily loads (TMDLs) are required for pollutants violating these standards. The Consent Decree in the Georgia TMDL lawsuit required TMDLs for mercury in six south Georgia rivers by August 2000. This paper summarizes the scientific models and associated procedures used to develop these mercury TMDLs, with example calculations from the Upper Ochlockonee River. Three separate software tools were used to produce the mercury TMDLs: the Watershed Characterization System (WCS), a mercury delivery spreadsheet, and the water pollutant fate model Wasp5. The WCS takes wet and dry atmospheric deposition and calculates mercury concentrations in soil as well as runoff and erosion fluxes to the stream system. Processes simulated include reduction and volatilization from the soil, runoff, and erosion of solids and associated mercury. The mercury delivery spreadsheet calculates the fraction of mercury from the landscape that is lost in the watershed's tributary system due to reduction and volatilization. Speciation of the watershed loadings between divalent and methyl mercury is based on site-specific data. The Wasp5 model takes the speciated loadings delivered from the watershed and from point sources, and calculates total and methyl mercury concentrations in the water column and sediments of the river channel. Processes simulated include advection, sediment exchange, reduction, volatilization, methylation, and demethylation in the water column, and methylation and demethylation in the sediments. The WCS model gives loadings by several categories. Total watershed loadings and delivery ratios using average tributary flows were used in Wasp5 to calculate expected average mercury concentrations. These concentrations were used as initial conditions in a short (6-month) simulation of recent mercury dynamics in the recent drought conditions. Direct dry deposition loadings to water surfaces were used with drought tributary flows to give estimated loadings delivered to the Ochlockonee River during summer 2000. Wasp5 calculations of mercury concentrations under these conditions compared reasonably well with observed data from surveys in July 2000. This offers some degree of confidence in the TMDL relating atmospheric nonpoint source and point source loadings to river mercury concentrations under average conditions.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Dai, T., Wool, T.A., and Ambrose, Jr., R.B. Development of a watershed-based mercury pollution characterization system. Presented at: Ecological Society of America Meeting, Madison, WI, August 5-10, 2001.

8/5/2001

Contact: Robert B. Ambrose

Abstract: To investigate total mercury loadings to streams in a watershed, we have developed a watershed-based source quantification model ? Watershed Mercury Characterization System. The system uses the grid-based GIS modeling technology to calculate total soil mercury concentrations and mercury loadings from direct atmospheric deposition, surface runoff, soil erosion and point sources. The input for the system includes land use, soil type, digital elevation, stream distribution, climate and atmospheric monitoring data. In addition, mercury reduction rate constant in the upper soil layer must be specified. The equations for mercury fate in soils were modified from a pollutant fate and transport model (IEM-2M) developed by U. S. Environmental Protection Agency. Using Watershed Mercury Characterization System, we calculated mercury loads in 20 sub-watersheds in the Savannah River watershed of Georgia and South Carolina. Sensitivity analyses indicate that mercury loading rates from this watershed are affected significantly by the atmospheric deposition flux, the proportion of impervious area, the proportion of direct water surface area, and the soil mercury reduction rate constant. Watershed Mercury Characterization System is distributed as a software extension for ArcView GIS.

Wommack, E., Shira, B.A., Avants, J., and Garrison, A.W. Bacterially-mediated degradation of a chiral disinfection byproduct. Presented at: American Society for Microbiology Annual Meeting, Orlando, FL, May 20-24, 2001.

5/20/2001

Contact: Arthur W. Garrison

Abstract: Disinfection of drinking and waste waters, through chlorination, can result in the production of chlorinated organic compounds, many of which are regulated by the U.S. Environmental Protection Agency. Among these regulated compounds are the haloacetic acids, which exhibit toxic effects in aquatic plants and algae and are believed to be carcinogenic. In waters containing trace levels of bromine, the chiral disinfection byproduct bromochloroacetic acid (BCAA) is commonly formed. Often times the enantiomers (stereoisomers) of chiral pollutant compounds exhibit dramatically different fates in the environment. That is, one enantiomer degrades quickly, while the other is recalcitrant to degradation. To examine the contribution of natural bacterial populations to BCAA degradation, a mesocosm study was performed using river water or mineral media amended with riverine bacterioplankton. BCAA enantiomers were separated and quantitated using capillary electrophoresis. Virio- and bacterioplankton abundance was determined by epifluorescence microscopy and bacterial community structure was ascertained using terminal restriction fragment analysis (T-RFLP) of 16S rDNA. The Microtox bacterial toxicity assay, which uses the luminescent marine bacterium *Photobacterium phosphoreum*, as well as direct counts, revealed the bacteriocidal character of BCAA. In mesocosms, BCAA degradation was almost entirely bacterially-mediated as sterile controls exhibited little degradation over the time course of the experiment. In general, BCAA degradation proceeded rapidly after an initial lag of 3 to 5 days. The fastest degradation was observed in bacterioplankton-amended mineral media in which BCAA was the sole carbon source. T-RFLP analysis of community 16S rDNA revealed significant shifts in bacterioplankton community structure after the addition of BCAA racemates. Overall, observations of BCAA degradation indicate that autochthonous bacterioplankton are critical in determining the fate of this chiral pollutant in aquatic environments.

Sawunyama, P., and Bailey, G.W. Interactions between organic compounds and cyclodextrin-clay systems. Presented at: 222nd American Chemical Society National Meeting, Chicago, IL, August 26-30, 2001.

8/26/2001

Contact: George W. Bailey

Abstract: Computational and experimental techniques are combined in order to better understand interactions involving organic compounds and cyclodextrin (CD)-clay systems. CD-clay systems may have great potential in the containment of organic contaminants in the environment. This study was undertaken in an effort to determine the extent of adsorption and/or complexation of a model organic compound, methyl orange (MO), in CD-clay systems. The anion form of MO interacts with the clay surface via cationic bridges whereas the cation form is weakly adsorbed by a cation exchange mechanism. In the presence of CD, complexation of MO by CD prevails over MO adsorption by the clay. In acidic media, the presence of CD has a profound influence on the competition between the clay and methyl orange for H⁺ ions. Also, calculations show that the interactions between clay and CD are minor - - predominantly weak van der Waals interactions.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Collette, T.W., and Williams, T.L. The role of Raman spectroscopy in the analytical chemistry of potable water. Presented at: 222nd American Chemical Society National Meeting, Chicago, IL, August 26-30, 2001.

8/26/2001

Contact: Timothy W. Collette

Abstract: Advances in instrumentation are making Raman spectroscopy the tool of choice for an increasing number of chemical applications. For example, many recalcitrant industrial-process monitoring problems have been solved in recent years with in-line Raman spectrometers. Raman is attractive for these applications for many reasons, including remote non-invasive sampling, minimal sample preparation, and tolerance of water. To a lesser extent, Raman spectroscopy is beginning to play a role in environmental analysis for the same reasons. At present, the environmental applications typically apply only to the most contaminated situations, due to still relatively high limits of detection. However, some emerging sampling technologies hold out the promise that Raman may soon be more widely applicable to the analytical chemistry of potable water. In this talk, we will discuss these recent advances and suggest avenues of future developments and applications that we expect to be most useful.

Collette, T.W., and Williams, T.L. Determination of perchlorate in some fertilizers and plant tissue by Raman spectroscopy. Presented at: 222nd American Chemical Society National Meeting, Chicago, IL, August 25-30, 2001.

8/25/2001

Contact: Timothy W. Collette

Abstract: We have successfully used Raman spectroscopy for the direct qualitative and quantitative analysis of perchlorate in fertilizer extracts without the need for chromatographic separation. This approach is attractive because Raman is not hindered by the presence of water or of high TDS, and it can be a definitive technique for qualitative identification. We have also applied this method to the identification of perchlorate in extracts of lettuce that have been grown in a greenhouse using irrigation water spiked with high levels (10 ppm) of perchlorate. Note that our goal is not to replace IC as the recommended method for the quantitative determination of perchlorate, but, instead, to provide a confirmatory technique to be used in conjunction with IC, particularly for samples exhibiting high TDS.

Weber, E.J., Kenneke, J.F., and Hoferkamp, L.A. Reactivity of chemical reductants as a function of redox zonation. Presented at: Third International Conference on Groundwater Quality, Sheffield, United Kingdom, June 18-21, 2001.

6/18/2001

Contact: Eric J. Weber

Abstract: To determine the distribution and reactivity of chemical reductants as a function of redox zonation, the reaction kinetics for a series of probe molecules have been measured in sediments for which redox conditions have been well characterized. redox characterization has included quantifying the major redox-active species in sediment pore waters (NO_3^- , Mn^{2+} , Fe^{2+} , SO_4^{2-} , S^{2-} , CH_4 , and H_2) and the use of acid extraction to determine the major pools of Fe(II) , Fe(III) , FeS and FeS_2 associated with the solid phase of the sediments. Reactivity patterns determined for halogenated methanes in iron-reducing and sulfate-reducing sediments and Fe(II) -goethite and FeS model systems suggest that Fe(II) sorbed to iron oxides is the dominant chemical reductant in both the iron-reducing and sulfate-reducing sediments. Reaction kinetics of a nitroaromatic probe chemical studied in sediments as a function of redox zonation provides further evidence for the important role of Fe(II) as a reductant in sediments under iron-reducing, sulfate-reducing and methanogenic conditions.

Ellington, J.J., and Evans, J.J. Effects of temperature and solvent composition on the CHIRALCEL OJ separation of chiral organophosphorus pesticides. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: James J. Ellington

Abstract: The separation of the enantiomers of twelve organophosphorus pesticides (OPs) was investigated on the CHIRALCEL OJ column to determine whether the mobile phase composition, flow rate and column temperature could be optimized to yield at least partial separation of the enantiomers of the 12 OPs. Chromatographic conditions were determined that gave either baseline or near baseline separations of the enantiomers of the twelve OPs on the CHIRALCEL OJ column. The separation of the enantiomers of eight OPs improved when the mobile phase content of the polar modifier was decreased to 4% or less and for one OP (trichloronate) to 0.0%. Column efficiency (resolution) increased for the enantiomers of two OPs at 40 °C and the peak 2/peak 1 area ratios decreased from 1.2 to nearly unity. The retention times were decreased by 50% for one pair of enantiomers when the column temperature was increased from 20 °C to 40 °C.

Jan 1, 2001 - Dec 31, 2001

Presented Published

11/11/2001

Ellington, J.J., Evans, J.J., Prickett, K.B., and Champion, W.L. HPLC separation of chiral organophosphorus pesticides on polysaccharide chiral stationary phases. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

Contact: James J. Ellington

Abstract: High-performance liquid chromatographic separation of the individual enantiomers of 12 organophosphorus pesticides (OPs) were obtained on polysaccharide chiral HPLC columns using an alkane-alcohol mobile phase. The OP pesticides were crotoxyphos, dialifor, dyfonate, fenamiphos, fensulfothion, isofenphos, malathion, methamidophos, profenofos, ruelene, tokuthion and trichloronate. The enantiomers of the twelve OPs were baseline resolved on at least one of the following columns: CHIRALPAK ADTM, CHIRALPAK ASTM, CHIRALCEL ODTM, CHIRALCEL OJTM, and CHIRALCEL OGTM. In continued method development, theseparation of the enantiomers of the twelve OPs was investigated more extensively on CHIRALCEL OJ to determine whether the mobile phase composition, flow rate and column temperature could be optimized to yield at least partial separation of the enantiomers. Chromatographic conditions were found that gave either baseline or near baseline separations of the enantiomers of the twelve OPs on the CHIRALCEL OJ column. Enzymatic degradation of several of the OPs was determined using a partially purified enzyme from Escherichia coli. The enzymatic degradation of the OP enantiomers was followed by HPLC using a CHIRALCEL OJTM column. The enzyme quickly degraded crotoxyphos enantiomers while dyfonate degradation took considerably longer. The enantiomers of both OPs were degraded at different rates. The enzyme did not degrade dialifor.

O'Neill, W., Jones, W.J., Whittemore, A., and Avants, J. Transformation of chiral pollutants in soil and sediment microcosms. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: William J. Jones

Abstract: The transformation rates and enantiomeric ratios of several chiral pollutants were determined in laboratory microcosms (25°C). Aerobic and anaerobic agricultural soil slurries were separately dosed with the following chiral pesticides: o,p'-DDT, o,p'-methoxychlor, cis-chlordane, trans-chlordane, heptachlor, heptachlor epoxide, and -HCH. In addition, microcosms prepared anaerobically with lake sediment were separately dosed with a polychlorinated biphenyl mixture (Arochlor 1260) and the chiral PCB congeners 2,2',3,4',5',6-hexachlorobiphenyl and 2,2',3,3',4,4',5,6-octachlorobiphenyl. Experimental treatments consisted of live (natural) slurries, live slurries dosed with an organic nutrient mixture, and autoclaved controls. The concentrations of the chiral pollutants in the experimental microcosms were analyzed by enantioselective high-resolution GC/MS and data were modeled to determine transformation rates. Enantiomer concentrations in transformed and unaltered (control) microcosms were compared to one another to assess enantioselective transformation of the compounds. Transformation was absent or insignificant in cis-chlordane, heptachlor epoxide, Arochlor 1260, and 2,2',3,3',4,4',5,6-octachlorobiphenyl dosed microcosms. However, appreciable losses of the parent compounds were observed in microcosms dosed with 2,2',3,4',5',6-hexachlorobiphenyl, o,p'-DDT, o,p'-methoxychlor, trans-chlordane, heptachlor, and -HCH. The addition of an organic nutrient mixture to the microcosms generally enhanced transformation rates, and transformation was greater in microcosms incubated under anaerobic conditions for all degraded compounds except -HCH. Statistically significant enantioselective transformation was not observed in most of the samples after 100 days incubation, but differences in enantiomeric ratios were observed in selected samples dosed with o,p'-DDT.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Sealock, G.A., and Wolfe, N.L. 2,4,6-Trinitrotoluene transformation in planted, soil columns. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: Nelson L. Wolfe

Abstract: 2,4,6-Trinitrotoluene (TNT), has been used extensively by the United States military to manufacture explosive devices. Since the conclusion of World War II, many of these military installations have also been involved in the disposal of surplus and outdated explosives. Both the commissioning and disposal of weapons at ammunition plants have led to soil, ground, and surface water contamination by munitions. It is estimated that munition contamination is found at approximately 50 military bases and explosives manufacturing facilities in the United States. In this study, the feasibility of using phytoremediation, the use of plants and the microbes associated with their rhizospheres to degrade contaminants, was examined. Two primary studies, a batch- scale kinetic study, and a vegetated, column study were conducted to determine the potential of various terrestrial plant species to transform TNT. For the kinetic study, plant tissue samples were submerged in a TNT solution and samples were extracted on a schedule of increasing time intervals for up to 30 hours. Sampling of the solutions occurred until non-detect levels were reached. All samples were characterized using liquid chromatography. Half- lives and degradation constants were calculated for first-order reactions with each plant species. In order to study TNT degradation in a plant-soil system, soil columns were constructed. A TNT sorption study was performed using the column soil. The data was fit using the Freundlich equation. A continuous input of 10 mg/L TNT was applied to the columns for two months. When application of TNT was concluded soil and plant tissue samples were obtained for TNT extractions. Soil samples were obtained at three depths. Plant samples consisted of leaf, stem, root, and tuber tissue. Soil extractions were conducted following EPA Method 8330. All species readily absorbed TNT from the soil. Some TNT transformation occurred in the soil as well as in the plant tissues. This was determined by the presence of TNT metabolites. No TNT or metabolites were found in leachates exiting the columns. The results of the study suggest that irrigation of TNT contaminated water is a viable option for remediation.

Garrison, A.W., Jones, W.J., Avants, J., and Jarman, J.L. Measurement of the enantioselective transformation of chiral pollutants by capillary electrophoresis. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: Arthur W. Garrison

Abstract: The enantiomers of chiral pollutants have identical physical and chemical properties but usually react selectively with enzymes or other chiral molecules. This enantioselectivity results in different rates of microbial transformation and differences in toxicity of the 2 (or more) enantiomers. To make more accurate risk assessments, it is necessary to understand the relative persistence and effects of the enantiomers; it follows that this understanding depends upon the ability to separate them. Enantiomeric separation can be accomplished by the use of chiral columns in GC and HPLC, and by chiral selectors in capillary electrophoresis (CE). This poster will describe techniques for enantiomer separation by CE, and show applications to environmental problems. Current studies involve CE to follow the loss of the enantiomers of dyfonate (an OP pesticide), imazaquin (an imidazolinone herbicide), and metalaxyl (an acylanilide fungicide) in soil slurries. CE, although less sensitive than GC or HPLC, has particular advantages that make it viable for following the transformation of chiral pollutants in benchtop experiments where the analyte can be dosed at a reasonably high concentration.

Hoehamer, C.F., and Wolfe, N.L. Biotransformation of 2,4,6-trinitrotoluene (TNT) by a plant-associated fungus *Fusarium oxysporum*. Presented at: 22nd Annual Society of Environmental Toxicology and Chemistry Meeting, Baltimore, MD, November 11-15, 2001.

11/11/2001

Contact: Nelson L. Wolfe

Abstract: The capability of a plant-associated fungus, *Fusarium oxysporum*, to transform TNT in liquid cultures was investigated. TNT was transformed into 2-amino-4, 6-dinitrotoluene (2-A-DNT), 4-amino-2, 6-dinitrotoluene (4-A- DNT), and 2, 4-diamino-6-nitrotoluene (2, 4-DAT) via 2- and 4-hydroxylamino-dinitrotoluene derivatives, which could be detected as intermediate metabolites. Transformation of TNT, 2-A- DNT, and 4-A-DNT was observed in whole cultures, as well as with the mycelium alone. Protein extracts were prepared from this fungus, and the concentrated cell-free extracellular culture medium was not capable of transforming TNT; however, low levels of TNT transformation were observed by a membrane fraction in the presence of NADPH under an argon atmosphere. A concentrated extract of soluble enzymes also transformed TNT, but to a lesser extent, under the same conditions. When TNT toxicity was studied with this fungus, a 50 % decrease in the growth of *F. oxysporum* mycelium was observed when exposed to 20 mg/l TNT.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Bouchard, D.C. Cosolvent effects on organic chemical partitioning to sediment organic carbon. Presented at: Society of Environmental Toxicology and Chemistry Organic Soil Contaminants Conference, Copenhagen, Denmark, September 2-5, 2001.

9/2/2001

Contact: Dermont Bouchard

Abstract: Sorption-desorption hysteresis, slow desorption kinetics and resultant bioavailability, and other nonideal phenomena have been attributed to the differing sorptive characteristics of the natural organic polymers associated with soils and sediments. The objectives of this study were to investigate the effects of a cosolvent, methanol, on sorption isotherm linearity with natural organic matter (NOM), and to evaluate whether these results support, or weaken, the rubbery/glassy polymer conceptualization of NOM. All of the sorption isotherms displayed some nonlinear character. Our data indicates that all of the phenanthrene and atrazine isotherms were nonlinear up to the highest equilibrium solution concentration to solute solubility in water or cosolvent ratios (Ce/Sw,c) used, approximately 0.018 and 0.070, respectively. Isotherm linearity was also observed to increase with volumetric methanol content (fc). This observation is consistent with the NOM rubbery/glassy polymer conceptualization: the presence of methanol in NOM increased isotherm linearity as do solvents in synthetic polymers, and suggests that methanol is interacting with the NOM, enhancing its homogeneity as a sorptive phase so that sorption is less bimodal as fc increases. The solubility parameter of methanol, 14.5 cal^{1/2} cm^{-3/2}, is within the range of solubility parameters estimated for NOM; hence, methanol would be effective at lowering the NOM glass transition temperature and enhancing isotherm linearity. When the equilibrium solution concentration was normalized for solute solubility in water or methanol-water solutions, greater relative sorption magnitude was observed for the methanol-water treatments, indicating greater sorptive uptake for the rubbery polymer fraction of NOM at similar time scales.

Ellington, J.J., and Wolfe, N.L. Phytoremediation: using plants to clean up contaminated soil, groundwater, and wastewater. Presented at: First Baltic Symposium on Environmental Chemistry, Tartu, Estonia, September 26-29, 2001.

9/26/2001

Contact: James J. Ellington

Abstract: Phytoremediation is an emerging cleanup technology for contaminated soils, groundwater, and wastewater that is both low-tech and low-cost. The cleanup technology is defined as the use of green plants to remove, contain, or render harmless such environmental contaminants as heavy metals, trace elements, organic compounds, and radioactive compounds in soil or water. Phytoremediation takes advantage of the unique and selective uptake capabilities of plant root systems together with the translocation, bioaccumulation, and contaminant storage/degradation abilities of the entire plant. Research in our laboratory indicates that plants can transform many organic contaminants in sediments, soils and natural waters to more environmentally acceptable products. Furthermore, plant enzyme systems have been shown to be stable in sediments and soils for long periods of time and still maintain their activity. The diagram illustrates the mechanisms for pollutant uptake by plants. Using the knowledge that some plants have a high enzymatic activity for breaking down chemical toxins in soils and surface waters will bring about hazardous waste technology that is both economical and environmentally friendly to clean up waste sites. The objectives of our research are to determine which plants contain the most effective enzyme systems for transforming chemicals to safer products and to develop and incorporate plant/enzyme mediated transformation algorithms into multimedia models. We want to quantitatively describe these processes through air, water and soil systems using molecular descriptors of the organic compounds and physical/chemical descriptors of the system to model plant mediated pollutant fate. Our approach has been to first identify the plants native to the site under consideration for phytoremediation. Native plants are harvested homogenized in the laboratory and the whole plant homogenate is fortified with the chemical(s) of interest. The fortified homogenate is monitored to determine extent of degradation of the chemicals. If degradation is observed, the stems, shoots, tubers, and roots are also assayed. Plants that are identified as degrading species are then evaluated in controlled greenhouse and field experiments. A second approach is to use axenically cultured plants to eliminate the possibility that microorganisms associated with the plant are responsible for the degradation. To date several plants (aquatic and terrestrial) have been identified as containing the enzyme that reacts to degrade 1,3,5-trinitrotoluene (TNT), a munition that contaminates many military sites. Another study has shown that many aquatic and land plants can degrade chlorine compounds. Still other plants including parrot feather (*Mariophyllum aquaticum*), duckweed (*Spirodela oligorrhiza*), and elodea (*Elodea canadensis*) have been shown to uptake and degrade organophosphate compounds such as pesticides to innocuous products. Results from a recent study based on using native cattails for remediation of a perchloroethylene plume will be discussed.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Bailey, G.W., and Sawunyama, P. Biosurfaces: a nonscale overview. Presented at: Soil Science Society of America Annual Meeting, Charlotte, NC, October 22-25, 2001.

10/22/2001

Contact: George W. Bailey

Abstract: Biosurfaces: A Nanoscale Overview. Environmental surfaces (mineral, organic, biological, and composite) determine the physicochemical and biological properties of soils and control the chemical reactivity, fate, transport and transformation of nutrients and chemical contaminants in soil ecosystems. In this paper we will examine the nature and character of biosurfaces --lignin, humics, polysaccharides, proteins, and cell walls of bacteria, fungi and algae. This will be done by scrutinizing the structure, morphology, chemical composition, chemical functionality, electronic properties, and hydrophobic/hydrophilic character of each biosurface type. Such scrutiny will be done through the "eyes" of scanning probe microscopy, spectroscopy, computational chemistry and virtual reality. Interpretation of such an examination will be couched in terms of a 3-dimensional, holistic, and dynamic perception of soil.

Earle, R., and Weaver, J.W. Simulation of a methyl tert-butyl ether (MTBE) plume with MODFLOW, MT3D and the hydrocarbon spill screening model (HSSM). Presented at: MODFLOW 2001 and Other Modeling Odysseys Conference, Golden, CO, September 11-14, 2001.

9/11/2001

Contact: James W. Weaver

Abstract: An MTBE plume in the Upper Glacial Aquifer of Long Island, NY was simulated by combining MODFLOW and MT3D with a semi-analytical model for a gasoline release. The first step was to develop and calibrate a 3-dimensional steady-state numerical ground water flow model of the aquifer using MODFLOW. The most important large scale features of the flow system that were captured in the MODFLOW model were the pattern of aerial recharge and the interaction of ground water with surface waters at one end of the plume. Historical site data and the observed contaminant distribution were then used to generate a gasoline release scenario that was simulated by the Hydrocarbon Spill Screening Model (HSSM). HSSM was used to simulate emplacement of gasoline over a three-year period and the resulting dissolution of MTBE into the aquifer. Both the MTBE concentration in ground water and the size of the source zone change with time as the fuel weathers and the lens expands. These results form a boundary condition for transport in the aquifer, which was simulated by using MT3D and the calibrated MODFLOW model. The simulation was in close agreement with field observations, including observed detachment of the MTBE plume from the gasoline source, and plume diving under the influence of aerial recharge.

Richardson, S.D., and Karst, U. A new tailor-made derivatizing agent for identifying polar carbonyl DBPs in drinking water. Presented at: 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

4/1/2001

Contact: Susan D. Richardson

Abstract: Although chlorine has been used to disinfect drinking water for approximately 100 years, there have been concerns raised over its use, due to the formation of potentially hazardous by-products. Ozone is a popular alternative to chlorine, however, there is still much not known about the disinfection by-products (DBPs) formed by ozone, particularly with regard to polar DBPs that may not be extracted and identified using conventional methods. We have recently utilized a new, tailor-made derivatizing agent designed and developed by Karst and coworkers to identify highly polar DBPs in ozonated drinking water. This reagent, 4-dimethylamino-6-(4-methoxy-1-naphthyl)-1,3,5-triazine-2-hydrazine (DMNTH), allows polar carbonyl DBPs to be detected by liquid chromatography (LC)/atmospheric pressure chemical ionization (APCI)-mass spectrometry at part-per-trillion levels, with no preconcentration.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Simmons, J.E., Richardson, S.D., Speth, T.F., Miltner, R.J., Schenck, K.M., Rice, G., Teuschler, L.K., Krasner, S.W., and Weinberg, H. Integrated technology-based toxicology studies on drinking water disinfection byproducts (DBPs). Presented at: Workshop on Application of Technology to Chemical Mixture Research, Fort Collins, CO, January 8-11, 2001.

1/8/2001

Contact: Susan D. Richardson

Abstract: DBPs are formed by reactions of chemical disinfectants with natural organic matter in the source water. Although more than 300 DBPs are known, many remain unidentified; for chlorination, known DBPs account for ~50% of the mass of total organic halide. Toxicological evaluation of these complex DBP mixtures is a critical data gap; therefore, ORD/U.S. EPA has developed a research plan for joint chemical and toxicological characterization of real-world complex mixtures obtained by concentration of drinking water disinfected either by chlorination (post-chlorination) or by ozonation (pre-ozonation/post-chlorination) processes. In vivo and in vitro toxicological assessments are planned with a targeted focus on reproductive and developmental endpoints, including other target organs to the extent possible. Experiments have been conducted to 1) develop methods for reverse osmosis (RO) concentration of water spiked with bromide and iodide, 2) perform extensive chemical analysis of DBPs expected to be present at very low concentrations (in the ppt range) and 3) study the chemical stability of the concentrated water. RO samples were extracted with XAD resins and analyzed by advanced GC/MS techniques (high and low resolution electron ionization and chemical ionization mass spectrometry). An attempt was made to comprehensively identify all DBPs present. Many DBPs were identified, including brominated and iodinated compounds, such as bromo- and iodo-trihalomethanes and -acetaldehydes, halonitromethanes, halopropanones, halonitriles, and haloacetamides. Although pre-ozonation/post-chlorination did form a number of halogen-containing byproducts, they were fewer in number and lower in concentration than formed by post-chlorination. (This abstract may not reflect EPA policy.)

Weaver, J.W. Localized recharge influences on MTBE transport and well placement considerations. Presented at: 17th Annual International Conference on Contaminated Soils, Sediments and Water, Amherst, MA, October 21-25, 2001.

10/21/2001

Contact: James W. Weaver

Abstract: Vertical characterization of a gasoline release site at East Patchogue, New York showed that methyl tert-butyl ether (MTBE) and aromatic plumes "dived" as they passed beneath a sand pit. That this behavior was caused by aquifer recharge was shown by two pieces of evidence. First by conducting a detailed investigation of hydraulic conductivity variation in wells on either side of the sand pit it was shown that no preferential flow paths exist. Second, by modeling flow in the aquifer, the pattern of recharge in the aquifer was shown to be sufficient to cause the observed vertical migration of the plumes. The model, available as an calculator on the EPA web site (<http://www.epa.gov/athens/onsite>), is based on an analytical solution of the flow equation and the theory of three-dimensional streamlines in Dupuit flow. As further confirmation the model has been shown to reproduce observed plume diving patterns at similar sites on Long Island. These sites provide confirmation of the concepts and the ability to develop models to reproduce field behavior. From this work cost-effective approaches for site characterization could be developed that include model forecasts of plume diving to determine well screen placement. For design of sampling networks additional capabilities must be included in the model, because of unusual features of the Long Island sites: established, well-characterized plumes and unique hydrogeologic characteristics. For sites without existing data there is a need to expand the model to include contaminant transport. By using the estimated release date and transport time to the recharge zones it can be determined if a plume is likely to be affected by the feature. This capability has been added to the calculator and compared against data from the East Patchogue site. Further work is underway on building more flexibility in the flow model.

Frick, W.E. Auto-expansive flow. Presented at: 2001: An Ocean Odyssey Meeting, Mar del Plata, Argentina, October 21-28, 2001.

10/21/2001

Contact: Walter E. Frick

Abstract: Physics suggests that the interplay of momentum, continuity, and geometry in outward radial flow must produce density and concomitant pressure reductions. In other words, this flow is intrinsically auto-expansive. It has been proposed that this process is the key to understanding turbulence as it will induce inflow and mixing in turbulent boundary layers. However, the theory contradicts the common assumption that velocity divergence term in the continuity relation may be neglected in modeling low Mach number turbulence. In other words, water is claimed to be dynamically incompressible. A rigorous compressible analysis of radial flow between two disks in water proves that the flow is predicted to be auto-expansive and that the divergence of velocity is significantly non-zero. The solution is compatible with the equation of state whereas the incompressible solution can be shown to be inconsistent with it and with the first law of thermodynamics. The work supports the basis for an auto-expansive model of turbulence.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Richardson, S.D., and Furlong, E.T. Emerging contaminants: what are the current hot environmental pollutants and what is next?. Presented at: Federation of Analytical Chemistry and Spectroscopy Societies Conference, Detroit, MI, October 7-12, 2001.

10/7/2001

Contact: Susan D. Richardson

Abstract: Much has been achieved in the way of environmental protection over the last 30 years. Laws have been passed that have improved the quality of our rivers and streams, the quality of the air we breathe, and the quality of the water we drink. However, as we learn more, new concerns arise. This presentation will detail chemical and microbial contaminants that are of current concern to the U.S. Environmental Protection Agency (EPA) and other agencies. Many of these contaminants of current concern (CCCs) are endocrine disrupting chemicals (EDCs). Synthetic chemical classes in this CCC category directly or indirectly introduced into the environment include pharmaceuticals, pesticides, surfactants, methyl-t-butyl ether (MTBE), perchlorate, aluminum, organotins and nitrobenzene. Compounds formed directly or indirectly from anthropogenic activity include algal toxins and a range of newly identified drinking water disinfection by-products (DBPs), such as nitrosodimethylamine (NDMA), halonitromethanes, iodo-trihalomethanes, and brominated DBPs, such as the brominated forms of MX and bromodichloromethane. Although not chemical contaminants per se, pathogenic microorganisms, such as *Cryptosporidium*, *Giardia*, *Legionella*, microsporidia, and *Helicobacter pylori*, are included because they co-occur with chemical contaminants and can have substantial effects on human health. Many of these contaminants have been proposed for consideration under the Unregulated Contaminants Monitoring Rule, which requires EPA to select five or more contaminants every five years to consider for regulation. In 1998, a Contaminant Candidate List (CCL) was established, which explicitly identifies drinking water contaminants that might be regulated by EPA at a future date. Methods are available for many of the proposed contaminants; however, several contaminants do not have rugged, reliable methods. These issues will also be discussed.

Richardson, S.D. The role of GC/MS and LC/MS in the discovery of drinking water disinfection by-products. Presented at: 222nd American Chemical Society National Meeting, Chicago, IL, August 26-30, 2001.

8/26/2001

Contact: Susan D. Richardson

Abstract: Gas chromatography/mass spectrometry (GC/MS) has played a pivotal role in the discovery of disinfection by-products (DBPs) in drinking water. DBPs are formed when disinfectants, such as chlorine, ozone, chlorine dioxide, or chloramine, react with natural organic matter in the water. Following the initial discovery of the first DBP--chloroform--by Rook in 1974, GC/MS would become the key tool used for measuring these DBPs in water and for discovering other DBPs that were formed. Over the last 25 years, hundreds of DBPs have been identified, mostly through the use of GC/MS, which has spawned further health effects studies and regulations on some of the DBPs. More recently, liquid chromatography/mass spectrometry (LC/MS) has been used to try to uncover highly polar DBPs that most experts think have been missed by earlier GC/MS studies. The role that GC/MS and LC/MS has played in these discoveries will be presented.

Richardson, S.D., Thruston, Jr., A.D., Weinberg, H.S., and Krasner, S.W. A nationwide drinking water disinfection by-product occurrence study - identification of new and toxicologically significant compounds with mass spectrometry. Presented at: Federation of Analytical Chemistry and Spectroscopy Societies Conference, Detroit, MI, October 7-12, 2001.

10/7/2001

Contact: Susan D. Richardson

Abstract: Drinking water disinfection by-products (DBPs) are formed when disinfectants, such as chlorine, react with natural organic matter and bromide present in the water. Chloroform was the first DBP identified in drinking water (in 1974), and was subsequently shown (along with other trihalomethanes?bromodichloromethane, dibromochloromethane, and bromoform) to cause cancer in laboratory animals. In the 25 years following the discovery of chloroform, several hundred DBPs have been identified and reported in the literature. However, only a very few DBPs have been studied for adverse health effects. Because health effects studies are extremely expensive (\$1-2 million), it is not possible to simply test all DBPs that are reported. Also, it is not wise to test DBPs for which there is no quantitative occurrence information (to know how widespread a particular DBP was and at what concentrations it is present). Therefore, we have initiated a nationwide occurrence study to quantify "high priority" DBPs and to identify any new ones that have not been previously reported. The DBPs to be quantified were the result of a major effort by expert toxicologists who scrutinized all DBPs reported in the literature for probable adverse health effects (based on their chemical structures). The "top 50" DBPs resulting from this prioritization were included for this nationwide occurrence study. Drinking water samples are being collected across the U.S. from waters that use chlorine, ozone, chlorine dioxide, or chloramine for disinfection. Preliminary results from this study will be presented.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Colarullo, S.J., Johnston, J.M., and Cyterski, M.J. Hydrologic elements of ecological risk in the Contentnea watershed, North Carolina. Presented at: American Geophysical Union Meeting, Boston, MA, May 29 - June 2, 2001.

5/29/2001

Contact: Susan J. Colarullo

Abstract:

Weaver, J.W., and Small, M.C. Decision-making, science and gasoline additives. Presented at: American Geophysical Union Fall Meeting, San Francisco, CA, December 10-14, 2001.

12/10/2001

Contact: James W. Weaver

Abstract:

Methyl-tert butyl ether (MTBE) has been used as a gasoline additive to serve two major purposes. The first use was as an octane-enhancer to replace organic lead, beginning in 1979. The second use, which began about 1992, was as an oxygenated additive to meet requirements of the Clean Air Act Amendments (CAAA) of 1990. Generally, the amount of MTBE used for octane enhancement was lower than that required to meet CAAA requirements. An unintended consequence of MTBE use has been widespread groundwater contamination. The decision to use certain amounts of MTBE or other chemicals as gasoline additives is the outcome of economic, regulatory, policy, political, and scientific considerations. Decision makers ask questions such as "How do ground water impacts change with changing MTBE content? How many wells would be impacted? and What are the associated costs?" These are best answered through scientific inquiry, but many different approaches could be developed. Decision criteria include time, money, comprehensiveness, and complexity of the approach. Because results must be communicated to a non-technical audience, there is a trade-off between the complexity of the approach and the ability to convince economists, lawyers and policy makers that results make sense. The question on MTBE content posed above was investigated using transport models, a release scenario and gasoline composition. Because of the inability of transport models to predict future concentrations, an approach was chosen to base comparative assessment on a calibrated model. By taking this approach, "generic" modeling with arbitrarily selected parameters was avoided and the validity of the simulation results rests upon relatively small extrapolations from the original calibrated models. A set of simulations was performed that assumed 3% (octane enhancement) and 11% (CAAA) MTBE in gasoline. The results were that ground water concentrations would be reduced in proportion to the reduction of MTBE in the fuel. Plume lengths, though, would not be proportionately reduced. One implication of these results was that the concentrations would be reduced, but the number of impacted wells would remain similar. Because the simulations included emplacement of the gasoline, dissolution from contact with flowing ground water and transient transport in the aquifer, a common-sense explanation of the results was difficult to construct. A simpler model was then used for the purpose of explaining to policy makers why the plume length reductions were less than proportionate to the reduction of the amount of MTBE. The model was simple enough (one-dimensional, steady state, constant source concentration) so that the effect of each term of the transport equation on plume length could be easily shown. The weight of evidence from using multiple models, direct explanations from the transport equation, and field observation, then provided a sufficient basis for policy makers to understand scientifically how gasoline composition affects ground water impacts.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Kraemer, S.R. Subsurface residence times as an algorithm for aquifer sensitivity mapping: testing the concept with ground water models in the Contentnea Creek basin, North Carolina, USA. Presented at: MODFLOW 2001 and Other Modeling Odysseys Conference, Golden, CO, September 11-14, 2001.

9/11/2001

Contact: Stephen R. Kraemer

Abstract: This poster will present a modeling and mapping assessment of landscape sensitivity to non-point source pollution as applied to a hierarchy of catchment drainages in the Coastal Plain of the state of North Carolina. Analysis of the subsurface residence time of water in shallow aquifers is useful for assessing the impact of fair weather loadings of non-point source pollution to streams, such as the drainage of nitrogen from agricultural fields via baseflow. While accurate prediction of pollution transport and transformation continues to challenge the most advanced methods of site characterization and computer modeling, the theoretical residence time distribution in shallow "groundwatersheds" offers the possibility of integrating complex heterogeneity into a relatively simple function. The key determinants of the robustness of simple residence time functions (i.e., recharge rate N , porosity n , saturated thickness H) are scale dependent in representation. We use GIS and ground water flow models to test and assess the influence of scale and heterogeneity on subsurface residence times. The hierarchical scales of investigation range from site scale (Lizzie, NC, 1.5 km²), to subwatershed scale (Sandy Run/Middle Swamp, 14-digit HUC, 125 km²), to watershed scale (Little Contentnea Creek, 11-digit HUC, 525 km²) to basin scale (Contentnea Creek, 8-digit HUC, 2579 km²). The Lizzie site provides an opportunity to test simplified geologic conceptual models against observed complexity. A back-of-the-envelope analysis using the comprehensive potential builds understanding of the flow between the surficial aquifer, the confined aquifer, and the stream alluvium. The finite difference model MODFLOW and the analytic element model GFLOW are used to solve for the two-dimensional flow field and define the groundwatershed at the Sandy Run/Middle Swamp scale. The release of a grid of tracers and their collection at the catchment outlet provides the quantification of the relative cumulative residence time distribution $F(T)$. This distribution can be approximated by $F(T) = 1 - \exp(-T/T)$, where $T = nH/N$, provided the aquifer is piece-wise constant in the properties making T , which is the average subsurface residence time. The Arcview GIS system is used to extrapolate the spatial distribution of average residence times for the Contentnea Creek basin. The effective zoning of residence times is presented as an aquifer sensitivity map of streams to fair weather loadings of non-point source pollution. The techniques presented are challenged by uncertainties in conceptual model and parameterization. Research continues on parameter estimation and quantifying uncertainty.

Frick, W.E. The Bernoulli equation and compressible flow theories. Presented at: American Geophysical Union Meeting, Fort Collins, CO, April 2-5, 2001.

4/2/2001

Contact: Walter E. Frick

Abstract: The incompressible Bernoulli equation is an analytical relationship between pressure, kinetic energy, and potential energy. As perhaps the simplest and most useful statement for describing laminar flow, it buttresses numerous incompressible flow models that have been developed to model turbulent flow. In a re-examination of the derivation, Frick (2001) shows that the Theorem of the Mean for Integrals, not the assumption of absolute incompressibility, is the underlying justification for the simplification that makes it possible to derive the Bernoulli equation from the Euler equation. In other words, the assumption of incompressibility is unnecessary and the equation actually represents a compressible relationship. While this finding supports the expansive turbulence model proposed by Frick, Emerman, and Sigleo (2001), a closer look at their derivation of flow between two disks suggests that the underlying approximations are not entirely consistent with the theory. In other words, the physics of the expansive turbulence model proposes that the divergence of the velocity is positive, which is not what their solution shows.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Frick, W.E. Predicting the buildup of pollutant concentrations using EPA's visual plumes model. Presented at: Estuarine Research Federation Meeting, St. Petersburg, FL, November 4-8, 2001.

11/4/2001

Contact: Walter E. Frick

Abstract: Anthropogenic sources contribute pollutants to estuaries that are significantly influenced by tides, frequently exhibiting velocity reversals. Flow reversals, even in the absence of diffusion, can cause a buildup of pollution from a particular discharge in the receiving water. On the flood, the receiving water is loaded with pollutants as it passes over the source and moves upstream. On the ebb tide, it passes over the discharge a second time. If the freshwater flow is small compared to the tidal flow, the process repeats several times and raises the ambient background pollution above the prevailing levels due to other sources or natural processes. The U.S. EPA's Visual Plumes model offers a way to estimate the buildup of background pollution from this process if the estuary is reasonably one-dimensional in character. The general approach is simple, ignoring dispersion and the effect of the channel details, except at the source. Besides describing source variables and physical conditions, such as ambient density stratification, input is limited to defining the cross-sectional area of the channel at the point of discharge and the water velocity as a function of time. The theory is described and examples of the technique are presented.

Frick, W.E. Visual plumes mixing zone modeling software. Presented at: Fifth International Marine Environmental Modelling Seminar, New Orleans, LA, October 9-11, 2001.

10/9/2001

Contact: Walter E. Frick

Abstract: The U.S. Environmental Protection Agency has a long history of both supporting plume model development and providing mixing zone modeling software. The Visual Plumes model is the most recent addition to the suite of public-domain models available through the EPA-Athens Center for Exposure Assessment Modeling (CEAM) web page. The Windows-based Visual Plumes adapts, modifies, and enhances the earlier DOS-based PLUMES with a new interface, models, and capabilities. Visual Plumes may be described as a public platform for mixing zone models designed to encourage the continued improvement of plume theory and models by facilitating verification and inter-model comparison. The approach implies that modeling consistency should be separated from the scientific process of model development by a protocol for specifying official models for specific flow classes and periods of time. Some examples are presented to illustrate Visual Plumes' new capabilities. For example, it offers an algorithm for estimating the buildup of background pollution from the re-circulation of previously contaminated receiving water in reasonably one-dimensional estuaries. It features bacterial decay models that estimate temporal changes in first-order decay rates based on environmental stresses, including solar insolation, absorption (depth), salinity, and temperature. The basis for these capabilities is the optional linkage to time-series input files that allows Visual Plumes to simulate mixing zone and far-field parameters for long periods. Visual Plumes' application to OCS oil exploration discharges is also discussed. Examples illustrate these and other unique capabilities. Information is also provided on obtaining guidance useful for accessing this additional modeling power, including the description of mixing zone courses conducted in Alaska, California, Oregon, and Washington since Visual Plumes passed peer review last year.

Jan 1, 2001 - Dec 31, 2001

Presented Published

BOOK CHAPTER

Johnston, J.M. "A scientific and technological framework for evaluating comparative risk in ecological risk assessments." In: Modelling of Environmental Chemical Exposure and Risk Dordrecht, The Netherlands: Kluwer Academic Publishers 2001, 133-150.

1/15/2001

Contact: John M. Johnston

Abstract: There are significant scientific and technological challenges to managing natural resources. Data needs are cited as an obvious limitation, but there exist more fundamental scientific issues. What is still needed is a method of comparing management strategies based on projected impacts to ecosystem health. Ecological risk assessment is a field in its infancy, and its focus has been primarily toxic hazards (i.e. pesticides) to aquatic endpoints. Expanding on these achievements with the expression of sustainable, edible fisheries in an entire estuary as an assessment endpoint, and with greater complexity than a single species or species-by-species approach, is a first challenge. The extension of the scope of a risk assessment to include non-chemical stresses, such as land use change and nitrogen enrichment, is requisite to managing resources given the significance of how these disturbances alter hydrologic balances, habitat characteristics, and even the structure of ecological communities. The separation of intrinsic variability in the status of the fisheries from those variations that result from anthropogenic sources of disturbance is also a challenge that is not trivial. Management alternatives are thus evaluated based on the costs of remediation and related economic and societal issues and the projected changes in resource quality. Ultimately, terrestrial endpoints require attention as well. As an interdisciplinary application of such fields as ecology, biology, environmental management, toxicology, hydrology, and economics, ecological risk assessment requires a much broader, more comprehensive scope and a conceptual framework that synthesises the contributions of the supporting science and management. These challenges combine with the practical, technological challenges of how to conduct a risk assessment. Central to the goal of performing analyses of various resource management scenarios is the need for a computer-based problem solving environment that automates many of the associated tasks: data gathering and manipulation, integration of statistical, empirical, and mathematical simulation modelling and analysis techniques, and the accommodation of model inter-comparisons within a common framework. Because there are no rules as such for performing an ecological risk assessment, the guidelines that exist as expert knowledge could also be codified and made available within such a framework. It is important to understand that such a framework is much more than simply a collection of assorted tools in a software toolkit. It is the implementation of the science for performing comparative ecological risk. Advances in ecological risk assessment are of a scientific as well as technological nature, and any hoped for state-of-the-art applications of the field must eventually give attention to both areas of need. I present the ongoing development of both a scientific conceptual model for performing comparative risk and a software framework to meet these needs.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Williams, T.L., and Collette, T.W. "Environmental applications of Raman spectroscopy to aqueous systems." In: Handbook of Raman Spectroscopy, Chapter 17 Lewis, I.R. and H.G.M. Edwards (Ed.), New York, NY: Marcel Dekker 2001, 683-731.

8/1/2001

Contact: Timothy W. Collette

Abstract: The aim of this chapter is to demonstrate the great potential that the Raman spectroscopic technique offers for environmental applications, particularly to aqueous systems. We demonstrate the benefits of the technique relative to other information-rich spectroscopic techniques, in light of the immense advances that have taken place in Raman instrumentation in the decade preceding this writing. Also, we provide our perspective on the current limitations of the technique and offer suggestions for potentially fruitful avenues of research and development for increasing the value of Raman spectroscopy (RS) for environmental applications. We will demonstrate the benefits of the technique by reviewing environmental applications of RS to aqueous systems. The most recent reviews that cover this area were published in the early 1980s by Lynch and Brown [1], Gracile et al. [2], and Van Haverbeke and Brown [3]. Since that time, instrumentation for RS has undergone much development and improvement, and this is reflected in the resurgence of this technique to addressing environmental problems in aqueous systems. Our discussion and review of research in this area includes normal Raman spectroscopy (NRS), resonance Raman spectroscopy (RRS), surface-enhanced Raman spectroscopy (SERS), and the coupling of these methods to various separation techniques. Typically, environmental analysis is categorized according to the media in which the analysis is made, namely air, water, and soil. Although the advantages of RS are perhaps most important for aqueous systems, the technique has also been widely applied to air analysis, especially in the remote analysis of pollutants, with a range of up to several kilometers. In fact, approximately 150 articles devoted to this topic have been published since 1990. Many of these studies involve Raman-based light detection and ranging (LIDAR). In particular, smoke-stack emission studies have been an area of considerable potential for these techniques and much of the work has involved simple inorganic species (e.g., NO, SO₂, NO₂, CO₂, and HS). Due to the extent of work in this area and the focus on the analysis of a limited set of simple inorganic chemical species, Raman-based LIDAR has developed into a mature field somewhat apart from the development of the general-purpose Raman spectrometer. For this reason, we have chosen to omit the development and application of Raman-based LIDAR (and related techniques) from our literature review and focus, instead, on aqueous systems. Moreover, LIDAR and related techniques have been reviewed thoroughly in recent years (e.g., see Panne et al. [4]). However, many of our comments that follow regarding the benefits of Raman (e.g., tolerance of water and high information content) apply to ambient-air analysis as well. Also, it should be noted that we have omitted nonlinear Raman techniques from our review and discussion. Although some of these techniques [most notably coherent anti-Stokes Raman spectroscopy (CARS) e.g., Refs. 5-8] show promise for environmental applications, progress in this has been slow.

Bailey, G.W., Akim, L.G., and Shevchenko, S.M. "Predicting chemical reactivity of humic substances for minerals and xenobiotics: use of computational chemistry, scanning probe microscopy and virtual reality." In: Humic Substances and Chemical Contaminants, Chapter 2 Clapp, C.E., M.H.B. Hayes, N. Senesi, P.R. Bloom, and P.M. Jardine (Ed.), Madison, WI: Soil Science Society of America 2001, 41-72.

12/1/2001

Contact: George W. Bailey

Abstract: In this chapter we review the literature on scanning probe microscopy (SPM), virtual reality (VR), and computational chemistry and our earlier work dealing with modeling lignin, lignin-carbohydrate complexes (LCC), humic substances (HSs) and non-bonded organo-mineral interactions. Graphical representations of SPM images, VR images of the structure and morphology of minerals and HSs, outcome of molecular mechanics (MM), molecular dynamics (MD) and simulated annealing calculations of these surfaces are presented via a CD ROM. Significant findings from these simulations include: (1) SPM provides the capability to investigate the structure and morphology of environmental surfaces; (2) VR software and animated computer graphics enhance our capability to visualize and interpret 3-D surface structures; (3) flexible linear polymers were found to undergo drastic conformational changes when approaching the mineral surface; (4) MD simulations suggest high stability of the organic polymer coatings on mineral surfaces; (5) sorption energies are compound-specific and depend on the sorbate-sorbent orientation; (6) humic polyanions bind to mica surfaces via cation bridges; and (7) computational chemistry provides the capability to simulate the chemical reactivity and energetics of environmental surfaces for chemical contaminants. We present an integrated methodology to simulate the chemical reactivity of minerals, HSs, organo-mineral aggregates and demonstrate an approach whereby we can study the interactions of xenobiotics with organo-mineral aggregate surfaces.

Jan 1, 2001 - Dec 31, 2001

Presented Published

7/1/2001

Hayter, E.J., and Gu, R. "Prediction of contaminated sediment transport in the Maurice River-Union Lake, New Jersey, USA." In: Coastal and Estuarine Fine Sediment Processes, Proceedings in Marine Science McAnally, W.H. and A.J. Mehta (Ed.), New York, NY: Elsevier Science 2001, 439-458.

Contact: Earl J. Hayter

Abstract: A sediment and contaminant transport model and its application to the Maurice River-Union Lake system in southern New Jersey, USA is described. The application is meant to characterize and forecast sediment and arsenic (As) distributions before and after proposed dredging activities. The model, HSCTM-2D, is a two-dimensional, depth-averaged, finite element code capable of simulating the hydraulics of both steady and unsteady surface water flows, cohesive and cohesionless sediment transport, and the transport and fate of inorganic contaminants. Interactions between dissolved (i.e., desorbed) and particulate (i.e., adsorbed) contaminants and sediments are accounted for by simulating the processes of adsorption and desorption of contaminants to and from sediments, respectively. Four model simulations yielded (As) flushing times ranging from 25 years for the "no action" scenario to four years for dredging of contaminant bed sediments in the Maurice River and Union Lake.

JOURNAL

Loux, N.T. Monitoring cyclical air-water elemental mercury exchange. Journal of Environmental Monitoring 3 (1):43-48 (2001). EPA/600/J-02/085.

1/30/2001

Contact: Nicholas T. Loux

Abstract: Previous experimental work has demonstrated that elemental mercury evasion from natural water displays a diel cycle; evasion rates during the day can be two to three times evasion rates observed at night. A study with polychlorinated biphenyls (PCBS) found that diurnal PCB air/water exchange rates exceeded nocturnal exchange rates by 32%. Given that the exchange rates of both PCBs and elemental mercury are dominated by the resistance in the aqueous thin film at the air/water interface and that water column elemental mercury concentrations in natural water bodies also display a diel cycle (and water column PCB concentrations do not) the findings here suggest that PCBs can serve as a tracer to assess the relative contribution of diel atmospheric temperature variations on elemental mercury air/water exchange rates. Using previously published data describing water column elemental mercury concentrations and the previously published diel mercury evasion model, four evasion scenarios are examined within the context of monitoring air/water toxicant exchange: constant atmospheric temperatures and constant water column elemental mercury concentrations; variable atmospheric temperatures and constant water column elemental mercury concentrations; constant atmospheric temperatures and variable water column elemental mercury concentrations; and variable atmospheric temperatures and variable water column elemental mercury concentrations. A scenario of monthly elemental mercury air/water exchange also is examined (at constant atmospheric and water column elemental mercury concentrations). Some of the findings include: (1) atmospheric temperature variations do have a significant effect on air/water toxicant exchange; (2) diel atmospheric temperature variations become more significant to overall diel toxicant exchange rates the closer the air/water system is to equilibrium conditions; (3) for refractory toxicants, average diel exchange rates are best estimated by averaging datasets obtained over a 24 h period or, at minimum, by measuring exchange rates at average atmospheric temperature values; (4) for elemental mercury, variable diel water column concentrations are likely to be the dominant contributor to variations in diel evasion rates; (5) diel atmospheric temperature variations amplify the magnitudes of both diel mercury evasion and absorption events and can shift maximum evasion rates to later in the day; (6) variations in monthly elemental mercury air/water exchange rates may exceed diel variations; and (7) 24 h and monthly monitoring efforts will likely be required to accurately describe diel and annual elemental mercury air/water exchange in a given system.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Shi, W., Sun, M.Y., Molina, M., and Hodson, R.E. Variability in the distribution of lipid biomarkers and their molecular isotopic composition in Altamaha estuarine sediments: implications for the relative contribution of organic matter from various sources. *Organic Geochemistry* 32 (4):453-467 (2001). EPA/600/J-02/083.

4/1/2001

Contact: Marirosa Molina

Abstract: The estuarine mixing zone is an effective trap for particulate and dissolved organic matter from many sources, and thus greatly affects transport and deposition of organic matter between the land and ocean. This study examined sedimentary distributions of various fatty acids and their stable isotope compositions at three sites which represent different levels of mixing in the Altamaha River estuary, Georgia, USA. Distributions of other neutral lipids (phytol, C-14-C-32 fatty alcohols, and two sterols) were also determined as supplementary biomarkers from various sources. Results suggest that POM from terrestrial plant material was dominant at an initial, upper estuary mixing zone (salinity in the water column is near zero but porewater in the sediment is saline) while POM from marine sources was mainly deposited at a more intensive mixing zone (when salinity in surface and bottom waters was identical) in the Altamaha. Much less particulate lipid was deposited in Altamaha River mouth sediments even during the high discharge season, suggesting that terrestrial plant-derived POM may not be significantly transported across the mixing zone. Analyses of fatty acid isotopic composition further verify the differential deposition pattern of POM from different sources.

Loux, N.T., and Anderson, M.A. Mobil ion activities at charged interfaces. *Colloids & Surfaces A: Physicochemical & Engineering Aspects* 177 (2/3):123-131 (2001). EPA/600/J-02/086.

2/28/2001

Contact: Nicholas T. Loux

Abstract:

Opsahl, S.P., Jones, J.W., and Zepp, R.G. Photochemically-induced alteration of stable carbon isotope ratios (δ C-13) in terrigenous dissolved organic carbon. *Geophysical Research Letters* 28 (12):2417-2420 (2001). EPA/600/J-02/102.

6/15/2001

Contact: Richard G. Zepp

Abstract: Exposure of riverine waters to natural sunlight initiated alterations in stable carbon isotope ratios (δ C-13) of the associated dissolved organic carbon (DOC). Water samples were collected from two compositionally distinct coastal river systems in the southeastern United States-the Satilla River which has high DOC concentrations (10-35 mg/l), and the Altamaha River which has relatively low DOC concentrations (3-9 mg/l). Approximately 21-26% of the DOC was remineralized to DIC. The δ C-13 of remineralized DIC was isotopically "light" (δ C-13 = -28.8 to -33.2 parts per thousand) relative to the initial DOC (δ C-13 = -27.4 parts per thousand), leaving a residual fraction of isotopically "heavy" (δ C-13 = -25.8 to -26.6 parts per thousand) DOC. Photochemically-induced fractionation of C-13 results from selective degradation of certain biochemical constituents including lignin phenols. These results are consistent with shifts in VC of DOC observed during mixing of river and marine waters, suggesting that photochemically-induced alterations are a factor in determining these changes.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Anderson, S.L., Machula, J., Cherr, G., Zepp, R.G., Santavy, D.L., Hansen, L.J., and Mueller, E. Indicators of UV exposure in corals and their relevance to global climate change and coral bleaching. Human and Ecological Risk Assessment 7 (5):1271-1282 (2001). EPA/600/J-02/101.

10/1/2001

Contact: Richard G. Zepp

Abstract: A compelling aspect of the deterioration of coral reefs is the phenomenon of coral bleaching. Through interactions with other factors such as sedimentation, pollution, and bacterial infection, bleaching can impact large areas of a reef with limited recovery, and it might be induced by a variety of stressors including temperature and salinity extremes, and ultravioletlight. Under conditions of ocean warming, often associated with calm and stratified waters, photobleaching of UV-absorbing chromophoric dissolved organic matter (CDOM) is increased, and penetration of both UV-B. and UV-A is greatly enhanced. Indices of UV-specific effects in coral tissue are needed to test whether UV increases, associated with global climate change, are harmful to corals. To address this challenge, we have evaluated UV-specific effects in corals and have characterized factors that alter penetration of UV radiation over coral reefs. An immunoblotting assay was developed to examine UV-specific lesions (thymine dimers) in coral and zooxanthellae DNA. We observed dose-dependent increases of thymine dimers in coral (*Porites porites* var *porites*) exposed to artificial solar irradiance in a solar simulator, although effects were not strictly proportional. UV measurements were made in July 1999 at Eastern Sambo reef and nearby sites, including profiling along transects from reef to shore. Results of these analyses indicate that the coral at Eastern Sambo reef (at 34 meters) were receiving UV-B radiation that was equivalent to 25 to 30% of surface UV irradiance. However, the water just inside the reef in Hawk Channel (located closer to land) was considerably more opaque to UV. This water photobleached with loss of UV absorbance and fluorescence when it was exposed to simulated solar radiation. These results indicate that photobleaching of the DOM and transport of near-shore water out over the reefs might play a key role in controlling UV penetration to the reef surface.

Mazur, C.S., and Jones, W.J. Hydrogen concentrations in sulfate-reducing estuarine sediments during PCE dehalogenation. Environmental Science & Technology 35 (24):4783-4788 (2001). EPA/600/J-02/088.

12/15/2001

Contact: William J. Jones

Abstract: Despite recent progress made evaluating the role of hydrogen (H₂) as a key electron donor in the anaerobic remediation of chloroethenes, few studies have focused on the evaluation of hydrogen thresholds relative to reductive dehalogenation in sulfidogenic environments. Competition for hydrogen exists among microbial populations in anaerobic sediments, and direct evidence indicates that lower hydrogen thresholds are observed with more energetically favorable electron-accepting processes. This study examined aqueous hydrogen concentrations associated with sulfate reduction and perchloroethylene (PCE) dehalogenation in anoxic estuarine sediment slurry microcosms and evaluated the competition for H₂-reducing equivalents within these systems. After an initial lag period of 13 days, PCE was reductively transformed to trichloroethylene (TCE). During the time of continuous PCEdehalogenation, a significantly (P < 0.05) lower hydrogen concentration (0.5 nM) was observed in the sediment slurries amended with PCE as compared to slurries without PCE (0.8 nM). Sulfate reduction to sulfide was observed in all sediment slurries, but in microcosms actively dechlorinating PCE, the amount of reducing equivalents directed to sulfate reduction was approximately half the amount in sediment slurries without PCE. These findings provide evidence that a lower hydrogen threshold exists in anoxic estuarine sediment slurries with PCE as a terminal electron acceptor as compared to sediment slurries in which sulfate reduction was the predominant electronaccepting process. Furthermore, our results utilizing the inhibitor molybdate indicated that H₂-utilizing methanogens may have the potential to effectively compete with dechlorinators for hydrogen when sulfate reduction is initially inhibited.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Ellington, J.J., Evans, J.J., Prickett, K.B., and Champion, W.L., Jr. High performance liquid chromatographic separation of the enantiomers of organophosphorus pesticides on polysaccharide chiral stationary phases. *Journal of Chromatography A* 928 (2):145-154 (2001). EPA/600/J-02/092.

9/14/2001

Contact: James J. Ellington

Abstract: High-performance liquid chromatographic separation of the individual enantiomers of 12 organophosphorus pesticides (OPs) was obtained on polysaccharide enantioselective HPLC columns using alkane-alcohol mobile phase. The OP pesticides were crotoxyphos, dialifor, fonofos, fenamiphos, fensulfothion, isofenphos, malathion, methamidophos, profenofos, crufomate, prothiophos and trichloronate. The enantiomers of fenamiphos, fensulfothion, profenofos and crufomate were separated on CHIRALPAK AD; the enantiomers of fenamiphos were also separated on CHIRALPAK AS; the enantiomers of methamidophos, crufomate and trichloronate were separated on CHIRALCEL OD; the enantiomers of crotoxyphos, dialifor, fonofos, malathion, prothiophos and trichloronate were separated on CHIRALCEL OJ; and the enantiomers of isofenphos were separated on CHIRALCEL OG. Baseline or partial separation of the enantiomers of six of these OP pesticides was obtained on CHIRALCEL OJ. In continued method development, the separation of the enantiomers of the 12 OPs was investigated more extensively on CHIRALCEL OJ to determine whether the mobile phase composition, flow-rate and column temperature could be optimized to yield at least partial separation of the enantiomers. Chromatographic conditions were found that gave either baseline or near baseline separations of the enantiomers of the 12 OPs on the CHIRALCEL OJ column.

Jones, W.J., and Ananyeva, N.D. Correlations between pesticide transformation rate and microbial respiration activity in soil of different ecosystems. *Biology and Fertility of Soils* 33 (6):477-483 (2001). EPA/600/J-02/087.

6/25/2001

Contact: William J. Jones

Abstract: Cecil sandy loam soils (ultisol) from forest (coniferous and deciduous), pasture, and arable ecosystems were sampled (0-10 cm) in the vicinity of Athens, GA, USA. Soil from each site was subdivided into three portions, consisting of untreated soil (control) as well as live and sterile samples treated with the fungicide metalaxyl and the herbicide propachlor at 10 mg kg⁻¹ soil. Pesticide transformation rate, basal respiration (basal) and substrate-induced respiration (SIR) rates, and microbial metabolic quotient (qCO₂) were measured for the initial application of metalaxyl [methyl-N-(2,6-dimethyl-phenyl)-N-(methoxyacetyl)-DL-alanine] or propachlor (2-Chloro-N-isopropyl-acetanilide) at 22 C and 60% water holding capacity. Positive correlations were found for the following: metalaxyl transformation rate constant (Kmet) and basal (r=0.73); Kmet and SIR (r=0.83); propachlor transformation rate constant (Kpr) and basal (r=0.89); and Kpr and SIR (r=0.91). Regression analysis of pesticide transformation rate and soil respiration activity, coupled with specific soil properties (pH, Corg, and clay content), revealed a positive correlation between K and SIR for Corg (r=0.88 and 0.98, for metalaxyl and propachlor, respectively). qCO₂s were not significantly different (P=0.05) in propachlor-amended and pesticide-free soils. Metalaxyl amendment resulted in a change in the ecophysiological status of the soil microbial community as expressed by qCO₂. The qCO₂ values in metalaxyl-amended soils were significantly greater (P=0.05) in pine forest (by 25%) and arable and pasture (by 20%) soils compared to unamended soils. Differences in qCO₂ values may represent the magnitude of pesticide-induced disturbance. The duration of this disturbance was greater in the pine forest soil (48 days) compared to arable and pasture soils (21 and 15 days, respectively).

Ellington, J.J., Wolfe, N.L., Garrison, A.W., Evans, J.J., Avants, J., and Teng, Q. Determination of perchlorate in tobacco plants and tobacco products. *Environmental Science & Technology* 35 (15):3213-3218 (2001). EPA/600/J-02/091.

8/1/2001

Contact: James J. Ellington

Abstract: Previous field and laboratory studies with vascular plants have shown that perchlorate is transported from perchlorate fortified soils and is accumulated in the plant tissues and organs. This paper reports results of initial investigations on the accumulation of perchlorate in tobacco plants grown in soils amended with a fertilizer whose nitrogen content is derived, solely or in part, from mined Chile saltpeter (sodium nitrate). Methods were developed for the analysis of perchlorate in soils, tobacco leaves, and selected commercial tobacco products based on aqueous extractions from freeze-dried material. Analytical methods based on ion chromatography (IC), capillary electrophoresis (CE), and nuclear magnetic resonance (NMR) spectroscopy were developed for both qualitative and quantitative analyses of perchlorate. Results show that perchlorate is accumulated by tobacco plants into the lamina and midrib of the leaves from soils amended with Chile saltpeter which contains perchlorate as a natural impurity. Also, perchlorate can persist over an extended period of time and under a variety of industrial processes as shown by its presence in off-the-shelf tobacco products including cigarettes, cigars, and pouch and plug chewing tobaccos in concentrations ranging from 0.4 +/- 0.01 to 21.5 +/- 0.4 mg/kg.

Jan 1, 2001 - Dec 31, 2001

Presented Published

McCutcheon, S.C., and Rock, S.A. Phytoremediation: state of the science conference and other developments. Editorial introduction and special commentary. International Journal of Phytoremediation 3 (1):1-11 (2001). EPA/600/J-02/084.

5/7/2001

Contact: Steven C. Mccutcheon

Abstract: It is a pleasure to present six papers in this issue, selected from presentations at the U.S. Environmental Protection Agency (EPA) Conference, Phytoremediation: State of the Science held May 1-2, 2000 in Boston, MA, USA. These papers highlight some of the many advances reported in representative areas of phytoremediation. In addition to introducing the six papers that have undergone the standard International Journal of Phytoremediation (IJP) review, this special commentary also briefly (1) reviews the beginnings of phytoremediation to put the need for the 2000 EPA Conference venue into context, (2) reviews other advances presented at the conference, (3) notes where additional review and synthesis is necessary in context with the reports from other phytoremediation meetings and future developments.

Sawunyama, P., and Bailey, G.W. Quantum mechanical study of the competitive hydration between protonated quinazoline and Li⁺, Na⁺, and Ca²⁺ ions. Journal of Physical Chemistry A 105 (42):9717-9724 (2001). EPA/600/J-02/098.

10/25/2001

Contact: George W. Bailey

Abstract: Hydration reactions are fundamental to many biological functions and environmental processes. The energetics of hydration of inorganic and organic chemical species influences their fate and transport behavior in the environment. In this study, gas-phase quantum mechanical calculations at the MP2/6-31G**//HF/6-31G* and B3LYP/6-311+G(2df,2p)//B3LYP/6-31G* levels of theory are used to interpret the local competition for water between protonated quinazoline (1,3-diazanaphthalene) and metal ions, i.e., Li⁺, Na⁺, and Ca²⁺, under very low water contents. Calculated enthalpies and free energies of hydration at 298.15 K, DeltaH(hyd)(298) and DeltaG(hyd)(298), respectively, for the reactions quinazoline + H₂O --> quinazoline hydrate and Mz⁺ + H₂O --> M(H₂O)(z⁺) show that hydration of metal ions is more favorable than hydration of the quinazoline species. At the MP2/6-31G**//HF/6-31G* computational level, DeltaH(hyd)(298) values range from 0.4 kcal mol⁻¹ for neutral quinazoline to -11.1 and -10.5 kcal mol⁻¹ for N1 and N3 protonated quinazoline monocations, respectively, while DeltaH(hyd)(298) = -39.3, -28.2, and -56.4 kcal mol⁻¹ for Li⁺, Na⁺, and Ca²⁺ ions, respectively. At the B3LYP/6-311+G(2df,2p)//B3LYP/6-31G* computational level, DeltaH(hyd)(298) = 6.9, -5.5, and -5.4 kcal mol⁻¹ for neutral,quinazoline, N1, and N3 protonated quinazoline monocations, respectively, while DeltaH(hyd)(298) values are -34.0, -23.4, and -55.7 kcal mol⁻¹ for Li⁺, Na⁺, and Ca²⁺ ions, respectively. Accordingly,DeltaG(hyd)(298) values indicate that although metal cations hydrate spontaneously, quinazoline species do not. In addition to hydration, direct reaction between quinazoline species and metal cations is also explored.

Yan, L., and Bailey, G.W. Sorption and abiotic redox transformation of nitrobenzene at the smectite-water interface. Journal of Colloid and Interface Science 241 (1):142-153 (2001). EPA/600/J-02/099.

9/1/2001

Contact: George W. Bailey

Abstract: The effect of the redox state of structural Fe on the surface reactivity of iron-bearing phyllosilicates in aqueous suspension was investigated using a molecular probe. For this purpose the structural Fe in montmorillonite and ferruginous smectite was chemically reduced by sodium dithionite in citrate-bicarbonate (CB) buffer solution under N₂ at 70 degreesC, with the excess reactants removed by washing and centrifugation. Nitrobenzene was chosen as an electron acceptor probe to react with unaltered and chemically reduced smectites. Nitrobenzene was transformed into aniline only in the presence of the reduced smectites. This abiotic reductive transformation depended on the concentration of the electron acceptor in solution and the total accessible structural Fe in smectites. As much as 40% of the crystal layer structural Fe of the reduced smectites was oxidized to Fe-III; these electrons migrated to the surfaces/edges and then were transported into the adjacent aqueous layer. No significant effect of the oxidation state of structural Fe on the sorption of nitrobenzene on smectites was observed, but the reduced smectites sorbed less aniline than the unaltered smectites. The electronic structure and molecular geometry of the probe were modified within the smectite-water interface. Reducing structural Fe in smectites perturbed the surface reactivity.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Sawunyama, P., and Bailey, G.W. Modeling the interaction of agrochemicals with environmental surfaces: pesticides on rutile and organo-rutile surfaces. Journal of Molecular Structure (Theochem) 541 (1-3):119-129 (2001). EPA/600/J-02/097.

5/31/2001

Contact: George W. Bailey

Abstract: Non-bonded interactions between model pesticides and organo-mineral surfaces have been studied using molecular mechanical conformational calculations and molecular dynamics simulations. The minimum energy conformations and relative binding energies for the interaction of atrazine, ametryn, prometon, 2,4-D and DDT with rutile, Beta-cyclodextrin, and a Beta-cyclodextrin?rutile aggregate, respectively, were obtained. Relative binding energies for the pesticides on the mineral surface were generally in the order 2,4-D>prometon>ametryn>atrazine>DDT. The favored binding conformation for 2,4-D and DDT was usually one in which the aromatic rings lay parallel to the surface. S-triazines adopted conformations in which the triazine ring was oblique to the surface. On a composite Beta-cyclodextrin-rutile surface, the binding energies did not decrease appreciably although most of the organic contaminants showed a strong preference for the pristine mineral surface.

Collette, T.W., Williams, T.L., and D'Angelo, J.C. Optimization of Raman spectroscopy for speciation of organics in water. Applied Spectroscopy 55 (6):750-766 (2001).

6/15/2001

Contact: Timothy W. Collette

Abstract: We describe herein a method for determining constants for simultaneously occurring, site-specific "microequilibria" (as with tautomers) for organics in water. The method is based in part on modeling temperature-variant Raman spectra according to the van't Hoff equation. Spectra are measured with a charge-coupled device (CCD)-based, dispersive Raman spectrometer. The success of the method depends on accurate quantification of small spectral changes that are monotonic with temperature due to changes in relative concentration of equilibrium components. The method assumes that we can neglect intensity and frequency fluctuations in spectra collected over a period of days that are not due to chemical compositional changes (e.g., frequency shifts due to ambient instrument temperature fluctuations). Also, the method assumes that we can neglect the temperature dependence of the Raman spectrum of an individual conformer. We have investigated these assumptions and found that we can typically reduce frequency and intensity fluctuations to tolerable levels by normalizing all spectra on the basis of the atmospheric N₂ stretching band at 2331 cm⁻¹, which is observed in all of our spectra. Further, we have found that we can typically neglect the temperature dependence of Raman spectra if areas of depolarized bands are used in the modeling.

Sawunyama, P., Jackson, M., and Bailey, G.W. Interactions of methyl orange with cyclodextrin/sodium-montmorillonite systems probed by uv-visible spectroscopy. Journal of Colloid and Interface Science 237 (2):153-157 (2001). EPA/600/J-02/100.

5/15/2001

Contact: George W. Bailey

Abstract: Clay mineral colloids play important roles in the adsorption of polar organic contaminants in the environment. Similarly, cyclodextrins (CD) can entrap poorly water-soluble organic compounds. A combination of CDs and clay minerals affords great opportunities to investigate simultaneously complexation and adsorption processes involving organic contaminants. In this work, we investigated in situ the extent of adsorption and/or complexation of a molecular probe, methyl orange (MO), in CD/sodium montmorillonite systems using UV-visible spectroscopy. The anion form of MO interacts with the clay surface via cationic bridges, whereas the cation form is weakly adsorbed by a cation-exchange mechanism. Further, in acidic media, there is a local competition between MO and the montmorillonite surface for H⁺ ions. This inhibits protonation of MO in the immediate vicinity of the clay. The presence of CDs, however, perturbs the favored process of proton scavenging by the clay. In particular, in Beta CD-clay systems, Beta CD-complexed MO can compete successfully with the clay for H⁺ ions. The shielding effect of Beta CD appears to play a key role in preventing the deprotonation of complexed MO.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Arnold, J.W., Boothe, D.H., and Bailey, G.W. Parameters of treated stainless steel surfaces important for resistance to bacterial contamination. Transactions of the ASAE 44 (2):347-356 (2001). EPA/600/J-02/096.

4/15/2001

Contact: George W. Bailey

Abstract: Use of materials that are resistant to bacterial contamination could enhance food safety during processing. Common finishing treatments of stainless steel surfaces used for components of poultry processing equipment were tested for resistance to bacterial attachment. Surface characteristics were evaluated to determine factors important for resistance. Disks of stainless steel were steel ball burnished, glass beaded, electropolished, acid dipped, sandblasted, or left untreated. After treatment, the disks were incubated with bacteria from chicken carcass rinses. Bacterial growth during surface exposure was monitored by spectrophotometry, and bacterial counts were measured by scanning electron microscopy (SEM). The morphology of the surfaces was analyzed by atomic force microscopy (AFM), using disks from each of the treatments in the SEM studies. Changes in root mean square (RMS) roughness, center line average, bearing ratio/area, and other measurements corresponded to changes in bacterial contamination. Electropolished stainless steel showed fewer bacteria and biofilm formations than the other surfaces. The elemental composition of the surface was not changed by electropolishing. This article is the first to show that AFM is a rapid method for predicting the potential resistance of a surface to bacterial contamination. These results will aid manufacturers and processors in comparing and selecting finishes that are cost effective and resistant to contamination.

Wong, C.S., Garrison, A.W., and Foreman, W.T. Enantiomeric composition of chiral polychlorinated biphenyl atropisomers in aquatic bed sediment. Environmental Science & Technology 35 (1):33-39 (2001). EPA/600/J-02/090.

1/15/2001

Contact: Arthur W. Garrison

Abstract: Enantiomeric ratios (ERs) for eight polychlorinated biphenyl (PCB) atropisomers were measured in aquatic sediment from selected sites throughout the United States by using chiral gas chromatography/mass spectrometry. Nonracemic ERs for PCBs 91, 95, 132, 136, 149, 174, and 176 were found in sediment cores from Lake Hartwell, SC, which confirmed previous inconclusive reports of reductive dechlorination of PCBs at these sites on the basis of achiral measurements. Nonracemic ERs for many of the atropisomers were also found in bed-sediment samples from the Hudson and Housatonic Rivers, thus indicating that some of the PCB biotransformation processes identified at these sites are enantioselective. Patterns in ERs among congeners were consistent with known reductive dechlorination patterns at both river sediment basins. The enantioselectivity of PCB 91 is reversed between the Hudson and Housatonic River sites, which implies that the two sites have different PCB biotransformation processes with different enantiomer preferences.

Weber, E.J., Colon, D., and Baughman, G.L. Sediment-associated reactions of aromatic amines: 1. Elucidation of sorption mechanisms. Environmental Science & Technology 35 (12):2470-2475 (2001). EPA/600/J-02/078.

6/15/2001

Contact: Eric J. Weber

Abstract: Sorption of aromatic amines to sediments and soils can occur by both reversible physical processes and irreversible chemical processes. To elucidate the significance of these sorption pathways, the sorption kinetics of aniline and pyridine were studied in resaturated pond sediment. Aniline and pyridine behaved quite differently in the sediment-water systems. The sorption kinetics of pyridine were quite fast, reaching equilibrium within 1-2 h. In contrast, the sorption kinetics of aniline were characterized by a rapid initial loss of aniline from the aqueous phase followed by a much slower rate of disappearance. The rapid initial sorption of aniline upon respiking after an equilibration period of 200 h, and results of sorption kinetic studies as a function of substrate concentration, demonstrated that sorptive sites were not being saturated at the nominal concentration of aniline. Sequential extraction of a sediment treated with C-14-labeled pyridine and aniline suggested that pyridine was bound primarily through a reversible cation-exchange process, whereas aniline sorbed through both cation-exchange and covalent binding processes. At longer reaction periods sorption became increasingly dominated by covalent binding. The reaction kinetics for the slow, irreversible sorption of aniline appeared to be limited by the reactivity and/or availability of covalent binding sites. The initial rate and extent of aniline sorption was pH dependent (sorption increased with decreasing pH). At pH values above the pK(a) of aniline, sorption kinetics for the slower, irreversible loss of aniline were independent of pH.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Williams, T.L., Martin, R.B., and Collette, T.W. Raman spectroscopic analysis of fertilizers and plant tissue for perchlorate. *Applied Spectroscopy* 55 (8):967-983 (2001). EPA/600/J-02/094.

8/15/2001

Contact: Timothy W. Collette

Abstract: Raman spectroscopy, without the need for prior chromatographic separation, was used for qualitative and quantitative analysis of 59 samples of fertilizers for perchlorate (ClO₄⁻). These primarily lawn and garden products had no known link to Chile saltpeter, which is known to contain perchlorate. Perchlorate contamination is emerging as an important environmental issue since its discovery in water resources that are widely used for drinking, crop irrigation, and recreation in the Western U.S. Approximately 90% of the 32 fertilizer samples acquired between November 1998 and January 1999 contained perchlorate, and of these, the level was typically high (500-8000 mg/kg). However, only two of the 27 fertilizer samples acquired from June 1999 to May 2000 contained perchlorate and at a lower level than previously observed (i.e., similar to 250-350 mg/kg). Raman spectroscopy was also applied to the qualitative identification of perchlorate in extracts of lettuce that had been grown in a greenhouse using irrigation water spiked (at 10 ppm) with perchlorate. Generally, with a fertilizer extract, detection limits were similar to 50 ppm for perchlorate with short spectral acquisition times (similar to 5 min). Quantitation was typically accurate to within 2 to 14%, with an average %CV (coefficient of variation) of 6.3 among replicate runs. We compare Raman spectroscopy to ion chromatography, which is the currently recommended method for perchlorate analysis.

Wong, C.S., Garrison, A.W., Smith, P.D., and Foreman, W.T. Enantiomeric composition of chiral polychlorinated biphenyl atropisomers in aquatic and riparian biota. *Environmental Science & Technology* 35 (12):2448-2454 (2001). EPA/600/J-02/089.

6/15/2001

Contact: Arthur W. Garrison

Abstract: The enantiomeric composition of polychlorinated biphenyl (PCB) atropisomers was measured in river and riparian biota (fish, bivalves, crayfish, water snakes, barn swallows) from selected sites throughout the United States by using chiral gas chromatography/mass spectrometry. Nonracemic enantiomeric fractions (EFs) were observed for PCBs 91, 95, 136, and 149 for aquatic and riparian biota from Lake Hartwell, SC, a reservoir heavily contaminated with PCBs, and for these congeners and PCBs 132, 174, 176, and 183 in river fish and bivalves nationwide. Fish and bivalves showed marked differences in EFs as compared to sediment found at the same sampling sites, thus suggesting that PCBs are bioprocessed in biota in a different manner from those found in sediment (e.g., reductive dechlorination). Species-dependent patterns in PCB EFs were observed, which suggest differences in the ability of different species to bioprocess PCBs enantioselectively, most likely by metabolism. The presence of nonracemic PCBs in fish and bivalves suggests greater metabolic degradation of PCBs in these organisms than indicated from previous achiral studies and underscores the powerful potential of chiral analysis as a tracer of environmental bioprocesses.

Collette, T.W. Prediction of molecular properties with mid-infrared spectra and interferograms. *Applied Spectroscopy* 55 (6):1067-1078 (2001). EPA/600/J-02/093.

8/15/2001

Contact: Timothy W. Collette

Abstract: We have built infrared spectroscopy-based partial least squares (PLS) models for molecular polarizabilities using a 97 member training set and a 59 member independent prediction set. These 156 compounds span a very wide range of chemical structure. Our goal was to use this well defined chemical property to test the breadth of application of a method whose end use is aimed at predicting poorly defined, environmentally important properties and activity parameters (e.g., microbial transformation rate constants). Separate models were built using gas-phase mid-infrared spectra, and, alternatively, their Fourier transformations (i.e., interferograms). The optimum spectrum- and interferogram-based models produced approximately the same error (root mean square deviation divided by the parameter value range) for the independent prediction set, 9.53 and 9.92 %, respectively. With spectrum-based models, we found that de-resolving the spectra from a point spacing of 6 cm⁻¹ to about 40 cm⁻¹ produced much lower error (under leave-one-out, cross-validation) when all 156 compounds were included, but much higher error when a model was built using a structurally narrow subset of the compounds (namely, 38 alkanes). Qualitative interpretation of the first PLS weight-loading vector from the spectrum-based model provided important information on the relationship between chemical structure and molecular polarizability.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Richardson, S.D. Mass spectrometry in environmental sciences. Chemical Reviews 101 (2):211-254 (2001). EPA/600/J-02/081.

1/16/2001

Contact: Susan D. Richardson

Abstract: This review covers applications of mass spectrometry to the environmental sciences. From the early applications of mass spectrometry to environmental research in the 1960s and 1970s, mass spectrometry has played an important role in aiding our understanding of environmental pollution and processes. Due to the tremendous amount of environmental research in the literature, this review must by necessity be selective. A brief historical perspective on the early impacts of mass spectrometry on environmental research will be presented, with the remainder of the review focusing mainly on the last 8-10 years of environmental research. Numerous papers and abstracts were consulted before choosing selected ones to present here. The organization of this review is somewhat different from most reviews that cover a shorter period of time. Air analyses are grouped together, and biological samples are grouped together, but because many of the same types of analytical methods were used for the measurement of pollutants in different media (e.g., drinking water, surface waters, groundwater, wastewater, and soils), those pollutants are organized into compound classes. For example, pesticide papers will be grouped together, and dioxin papers are grouped together. It is anticipated that this organization would be helpful to the environmental scientist who wants an update on the types of mass spectrometry methods used for a particular pollutant. Geological measurements are included in this review, and they can be found in the Inorganic Analyses section.

Tebes-Stevens, C.L., Espinoza, F., and Valocchi, A.J. Evaluating the sensitivity of a subsurface multicomponent reactive transport model with respect to transport and reaction parameters. Journal of Contaminant Hydrology 52 (1-4):3-27 (2001). EPA/600/J-02/080.

11/30/2001

Contact: Caroline T. Stevens

Abstract: The input variables for a numerical model of reactive solute transport in groundwater include both transport parameters, such as hydraulic conductivity and infiltration, and reaction parameters that describe the important chemical and biological processes in the system. These parameters are subject to uncertainty due to measurement error and due to the spatial variability of properties in the subsurface environment. This paper compares the relative effects of uncertainty in the transport and reaction parameters on the results of a solute transport model. This question is addressed by comparing the magnitudes of the local sensitivity coefficients for transport and reaction parameters. General sensitivity equations are presented for transport parameters, reaction parameters, and the initial (background) concentrations in the problem domain. Parameter sensitivity coefficients are then calculated for an example problem in which uranium(VI) hydrolysis species are transported through a two-dimensional domain with a spatially variable pattern of surface complexation sites. In this example, the reaction model includes equilibrium speciation reactions and mass transfer-limited non-electrostatic surface complexation reactions. The set of parameters to which the model is most sensitive includes the initial concentration of one of the surface sites, the formation constant (K_f) of one of the surface complexes and the hydraulic conductivity within the reactive zone. For this example problem, the sensitivity analysis demonstrates that transport and reaction parameters are equally important in terms of how their variability affects the model results.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Washington, J.W., and Cameron, B.A. Evaluating degradation rates of chlorinated organics in groundwater using analytical models. Environmental Toxicology and Chemistry 20 (9):1909-1915 (2001). EPA/600/J-02/079.

9/1/2001

Contact: John W. Washington

Abstract: The persistence and fate of organic contaminants in the environment largely depends on their rate of degradation. Most studies of degradation rate are performed in the lab where chemical conditions can be controlled precisely. Unfortunately, literature values for lab degradation studies often are orders of magnitude higher than for field-generated studies, calling into question the relevance of lab-generated values for characterizing the persistence of organic contaminants in the environment. Complicating analysis of this ostensible disparity between lab and field degradation values, field-generated values often do not account for effects of adsorption. Modeling with a newly derived analytical solution for first-order degradation coupled with advective losses and adsorption to solve for degradation constants is insensitive to uncertainties in field properties. Application to field data shows that accounting for advection and adsorption greatly affects the value of calculated degradation constants compared to disappearance constants, which do not account for these phenomena. In fact, degradation constants, calculated using these analytical solutions and field data, are in the range reported for lab-generated data. Using these analytical solutions, for the sulfate-reducing field conditions documented for this site, perchloroethene, trichloroethene, 1,1,1-trichloroethane, 1,1-dichloroethane, and chloroethane all degraded with half-lives ranging from 5 to 115 d. Consistent with other studies of sulfate-reducing conditions, cis-1,2-dichloroethene did not chemically degrade at a measurable rate. When nonaqueous phase 1,1-dichloroethane is present, down-gradient concentrations vary in an annual sinusoidal pattern, apparently because of seasonal variation in dilution from groundwater recharge.

Jan 1, 2001 - Dec 31, 2001

Presented Published

Richardson, S.D. Water analysis. Analytical Chemistry 73 (12):2719-2734 (2001).
EPA/600/J-02/082.

6/15/2001

Contact: Susan D. Richardson

Abstract: This review covers developments in Water Analysis over the period of 1999 to 2000. A few significant references that appeared between January and February 2001 are also included. Previous Water Analysis reviews have been very comprehensive, often including more than 500 references. This year, however, Analytical Chemistry is changing its approach to these reviews to only include 100 to 200 significant references, and to mainly focus on trends in analytical methods. This was a difficult task, as the scope of Water Analysis is inherently broad, encompassing analytical studies involving all types of contaminants—organic and inorganic, as well as microorganisms. Rather than choosing a sub-area to focus on, this review will still attempt to cover most areas, except with fewer references. As a result, this review was by necessity very selective, and not all good references could be discussed. Typically when there were two or more of the same type of analytical method developed for a particular set of analytes, only one was chosen as representative of the method. Also, in this review, there is more of a focus on the analytical methods themselves, and less on results from significant studies. Papers focusing on the treatment of pollutants are generally omitted, as are most health effects papers. The upside to including fewer references is that those included can be discussed in greater detail, and more attention can be given to trends and comparisons of new methods to former ones. Numerous abstracts were consulted before choosing the best ones to present here. If an abstract was generally unclear or ambiguous, it was generally excluded. If the subject matter of the abstract appeared to be of routine nature, with no new, significant findings, it was also generally excluded. A table of acronyms is included (Table 1) as a quick reference to the acronyms of analytical techniques and other terms discussed in this review. The overall trends in analytical methods for water analysis include a greater use of solid-phase microextraction (SPME); fast gas chromatography (GC) and liquid chromatography (LC) methods; more on-line coupling of separation and extraction with detection (such as ion chromatography (IC) coupled to inductively coupled plasma mass spectrometry (ICPMS), IC coupled to atmospheric pressure chemical ionization mass spectrometry (APCI-MS), solid phase extraction (SPE) coupled to LC/MS or GC/MS, and membrane introduction mass spectrometry (MIMS) coupled to fast-GC/MS; and increased use of capillary electrophoresis (CE), large-volume GC injection, and enzyme-linked immunosorbent assay (ELISA) techniques. As always, analytical techniques continue to 'push the envelope' for detection limits. Several papers reported here were able to achieve low ng/L detection limits, with some achieving pg/L limits. In general, there is an effort to create analytical methods that are faster, simpler, and more sensitive. SPME involves the use of a small fiber to extract organic analytes directly from water, followed by thermal desorption in a GC or solvent desorption for LC analyses. SPME has simplified extractions and eliminates the use of solvents when GC or GC/MS is used for detection. Fast-GC and fast-LC methods are enabling very rapid analyses, usually in less than 5 min, which allows a higher throughput of samples per day. The on-line coupling of extraction and detection (such as SPE-LC/MS) is streamlining analyses, shortening sample work-up times, and allowing the entire process to be automated. On-line derivatization methods are also being developed. LC and CE methods are enabling the analysis of highly polar compounds that were difficult or impossible to analyze previously. Large-volume GC injection has helped to lower detection limits somewhat, and ELISA methods continue to be developed for more compounds. Occasionally, a completely new and different analytical instrument or device will be developed that offers significant advantages for analyzing water samples. LC/electrospray ionization (ESI)-MS and matrix-assisted laser desorption ionization (MALDI)-time-of-flight (TOF)-MS are past examples of such techniques that have enabled the analysis of highly polar analytes and also microorganisms. This year, a new high-field asymmetric waveform ion mobility spectrometer (FAIMS) was the significant new development. This FAIMS instrument is interfaced to ESI-MS, and it works by separating gas phase ions at atmospheric pressure and room temperature. FAIMS has been shown to effectively reduce background ions that are inherent with ESI-MS, allowing lower detection limits particularly for compounds below 300 Da. Preconcentration is not required; water samples are diluted with methanol to enable an efficient ESI process and then injected directly. Because no chromatographic columns are involved (ions are separated by the tuning of a voltage on the FAIMS device to allow transmission of a selected ion), analysis times are shortened, and the cost per sample is low. Details about the FAIMS methods developed can be found later in this review.

Jan 1, 2001 - Dec 31, 2001

Presented Published

PUB REPORT

Burns, L.A. Probabilistic aquatic exposure assessment for pesticides 1: Foundations. 2001. EPA/600/R-01/071.

10/15/2001

Contact: Lawrence A. Burns

Abstract: Models that capture underlying mechanisms and processes are necessary for reliable extrapolation of laboratory chemical data to field conditions. For validation, these models require a major revision of the conventional model testing paradigm to better recognize the conflict between model user's and model developer's risk (as Type I and Type II errors) in statistical testing of model predictions. The predictive reliability of the models must be hypothesized and tested by methods that lead to conclusions of the form the model predictions are within a factor-of-two of reality at least 95% of the time. Once predictive reliability is established, it can be treated as a method error within a probabilistic risk assessment framework. This report, developed under APM 131 (Develop a Probability-Based Methodology for Conducting Regional Aquatic Ecosystem Exposure and Vulnerability Assessments for Pesticides), describes a step-by-step process for establishing the predictive reliability of exposure models. Monte Carlo simulation is the preferred method for capturing variability in environmental driving forces and uncertainty in chemical measurements. Latin Hypercube Sampling (LHS) software is under development to promote efficient computer simulation studies and production of tabular and graphical outputs. Desirable outputs include exposure metrics tailored to available toxicological data expressed as distribution functions (pdf, cdf) and, if needed, empirical distribution functions suitable for use in Monte Carlo risk assessments combining exposure and effects distributions. ORD numerical models for pesticide exposure supported under this research program include a model of spray drift (AgDisp), a cropland pesticide persistence model (PRZM), a surface water exposure model (EXAMS), and a model of fish bioaccumulation (BASS). A unified climatological database for these models is being assembled by combining two National Weather Service (NWS) products: the Solar and Meteorological Surface Observation Network (SAMSON) data for 1961-1990, and the Hourly United States Weather Observations (HUSWO) data for 1990-1995. Together these NWS products provide coordinated access to solar radiation, sky cover, temperature, relative humidity, station atmospheric pressure, wind direction and speed, and precipitation. By using observational data for the models, trace-matching Monte Carlo simulation studies can transmit the effects of environmental variability directly to exposure metrics, by-passing issues of correlation (covariance) among external driving forces. Additional datasets in preparation include soils and land-use (planted crops) data summarized for the State divisions of Major Land Resource Areas (MLRA), derived from National Resource Inventory (NRI)

SYMPOS/CONF

Krasner, S.W., Pastor, S., Chinn, R., Scrimanti, M.J., Weinberg, H.S., Richardson, S.D., and Thruston, Jr., A.D. The occurrence of a new generation of DBPs (beyond the ICR). Presented at: American Water Works Association Water Quality Technical Conference, Nashville, TN, November 11-15, 2001. 2001.

11/11/2001

Contact: Susan D. Richardson

Abstract: A nationwide survey of 12 full-scale treatment plants for disinfection by-products (DBPs) was initiated in the U.S. in 2000. Approximately 50 DBPs that rated a high priority for potential toxicity and were not included in the Information Collection Rule (ICR) are being quantified. Some of the halogenated DBPs detected in this study have included mono-, di-, tri-, and/or tetra- species of halomethanes (HMs) (including iodinated species); haloacetonitriles (HANs); halo ketones (HKs); haloacetaldehydes (HAs); and halonitromethanes (HNMs). As the presence of bromide resulted in a shift in speciation, THMs, HAAs, HANs, HKs, HAs, and HNMs were detected that were not in the ICR. Chloramination formed certain dihalogen-substituted DBPs (HAAs, HAs) preferentially over related trihalogenated species. In addition, chlorine dioxide produced dihalogenated HAAs. Although the use of alternative disinfectants (ozone, chlorine dioxide, chloramines) minimized the formation of THMs, certain dihalogenated DBPs formed at significant concentrations. Biologically active granular activated carbon (GAC) removed a wide range of halogenated DBPs. A number of DBPs (e.g., certain HAs) were not stable at alkaline pH levels, probably because of base-catalyzed hydrolysis.

Jan 1, 2001 - Dec 31, 2001

Weinberg, H.S., Krasner, S.W., and Richardson, S.D. Determination of new carbonyl-containing disinfection by-products in drinking water. Presented at: American Water Works Association Water Quality Technical Conference, Nashville, TN, November 11-15, 2001.

Presented Published

11/11/2001

Contact: Susan D. Richardson

Abstract: Only a subset of all disinfection by-products were targeted for an intense occurrence study during the Information Collection Rule. Among 50 additional compounds selected for study because of their potential for significant toxicity, a group of carbonyl-containing compounds is being investigated for their occurrence in and fate during drinking water treatment. This paper looks at methods that were developed for detecting their presence at nano-molar levels and presents preliminary results of their occurrence in drinking water treatment plants paired for their different treatment regimes of the same source water.